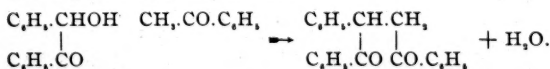


AMERICAN CHEMICAL JOURNAL

Contribution from the Kent Chemical Laboratory of the University of Chicago.
ON POTASSIUM CYANIDE AS A CONDENSING
AGENT.

BY ALEXANDER SMITH.

Some years ago I attempted to extend the use of potassium cyanide to other condensations than those resulting in the formation of aromatic ketols like benzoin. These were, at the time, the only cases in which it was effective. It was found that by its agency benzoin¹ and other ketols² could be easily combined with ketones, like acetophenone. The substances named gave desylacetophenone:



It was also found that benzoin interacted, under its influence, with benzalacetone³ forming a Δ^2 -keto-R-hexane derivative. The latter kind of action was subsequently seen to involve addition of benzoin to the double bond, and subsequent ring formation after the manner of the numerous syntheses carried out by Knoevenagel.⁴ It takes place more smoothly when

¹ J. Chem. Soc., 57, (1890) 643.

² Ber. d. chem. Ges., 26, (1892) 60.

³ J. Chem. Soc., 57, 644; Ber. d. chem. Ges., 26, 70.

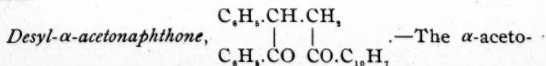
⁴ Ann. Chem. (Liebig), 281, (1894) 25.

sodium ethylate is used as a condensing agent and has been studied by Dr. J. B. Garner.¹

In 1891 Knoevenagel and Chalanay² observed that mandelic nitrile and benzyl cyanide in presence of potassium cyanide reacted to form diphenylsuccinic nitrile, with elimination of water. The former proposed to examine the condensing powers of the same reagent in other directions. On my previous work being brought to his attention, he, very courteously, left the further investigation of the field to me.

One or two aldol syntheses have been carried out with the help of the same condensing agent by Claisen³ and Kohn⁴.

Further experiments in the line originally pursued show that potassium cyanide is not so widely applicable as had been at first expected. In place of benzoin, substances like mandelic nitrile, benzoylcarbinol, furoin, and triphenylcarbinol have been used. For acetophenone there have been substituted acetomesitone, acetophenone, benzoylacetone, benzyl cyanide, camphor, fatty ketones, quinaldine, and other substances. The conditions of the experiment (boiling in diluted alcohol) have been altered in various ways. Fusing the substances without solvent and stirring with powdered potassium cyanide has been found frequently to improve the yield. Substitution of powdered potassium hydroxide in the latter method gave excellent results in one or two cases. With most of the possible pairs, from lists like the above, no condensation occurred, or pure products in sufficient amounts could not be isolated. Not wishing any longer to reserve this field, I now publish the few positive results. The 1:4 diketones described below were prepared with a view to the study of the action of phenylhydrazine upon them.



naphthone was prepared according to Claus⁵ and separated from the β -body by means of the picrates.⁶ The ketone (12

¹ Dissertation, Chicago, 1897.

² Ber. d. chem. Ges., 25, 294.

³ *Ibid.*, 25, 3164; Ann. Chem. (Liebig), 306, 322.

⁴ Monatsh. Chem., 19, 519.

⁵ Ber. d. chem. Ges., 19, 3180.

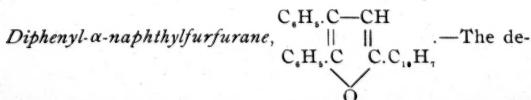
⁶ Rousset: Bull. chim. [3], 17, 313.

grams) and benzoin (17 grams) were dissolved in 50 per cent alcohol (100 cc.), potassium cyanide (2 grams) was added, and the solution was boiled with a reflux condenser for an hour. A turbidity, caused by the separation of an oil, appeared after twenty-five minutes, and, when the solution cooled, most of the product separated as a solid mass. This was extracted three times with boiling alcohol to remove the unchanged materials, and was then dissolved in 3.5 parts of boiling benzene, and precipitated by the addition of petroleum ether (b. p. 40°-60°). The product separated in stellate groups of white needles, which, when purified by repetition of the last process, melted at 151°. The yield was about 7 grams. Another mode of preparation, by fusion in presence of potassium hydroxide, is given below.

0.1851 gram substance gave 0.5814 gram CO₂, and 0.0958 gram H₂O.

	Calculated for C ₂₆ H ₂₀ O ₂	Found.
C	85.72	85.66
H	5.50	5.75

The substance is difficultly soluble in boiling alcohol, soluble in 3.5 parts of boiling benzene (less soluble in the cold), and insoluble in petroleum ether. Its constitution as a 1:4 diketone was determined by conversion into the corresponding furfurane, pyrrol, and thiophene compounds. The last, made by heating with phosphorus pentasulphide, melted at 93°. It was not analyzed.

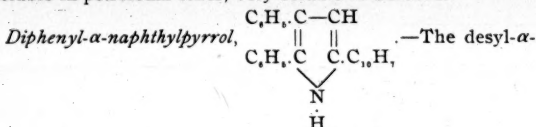


syl-α-naphthone (1 gram) was dissolved in cold concentrated sulphuric acid (10 cc.). The solution was allowed to stand for one hour and was then poured into water. The reddish solid which separated was recrystallized from petroleum ether, giving slender white needles melting at 96°.

0.1799 gram substance gave 0.5950 gram CO₂, and 0.0874 gram H₂O.

	Calculated for $C_{22}H_{18}O$.	Found.
C	90.17	90.20
H	5.20	5.40

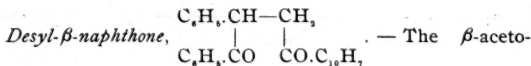
The substance was difficultly soluble in methyl alcohol, soluble in petroleum ether, very soluble in benzene.



naphthone was heated in a sealed tube with ammoniacal absolute alcohol at 200° – 220° for eight hours (at 150° – 170° little action had been found to take place). The liquid was evaporated and the product taken up with petroleum ether. The dark residue contained unchanged ketone. The solution was once more evaporated and the residue dissolved in alcohol. White needles (m. p. 122°) came out slowly. The substance did not give the red reaction with a pine splinter, but after a time the wood became bluish.

0.1790 gram substance gave 6.6 cc. N over 30 per cent KOH at 21° and 740 mm. (corr.).

	Calculated for $C_{22}H_{17}N$.	Found.
N	4.06	4.11



naphthone (1.8 grams), benzoin (2.3 grams), and potassium cyanide (0.4 gram), were dissolved in 50 per cent alcohol (20 cc.) and boiled with a reflux condenser for one and one-quarter hours. An oil separated and soon became solid. This solid was rubbed repeatedly with cold alcohol and finally freed from impurities by boiling with the same solvent, in which it is soluble with difficulty. The residue was recrystallized three times from benzene and, when pure, formed white needles melting at 155° .

0.1960 gram substance gave 0.6140 gram CO_2 , and 0.0990 gram H_2O .

	Calculated for $C_{20}H_{20}O_2$	Found.
C	85.72	85.43
H	5.50	5.65

It had been hoped that benzoylcarbinol, $C_6H_5.CO.CH_2OH$, on account of its resemblance to benzoin, would interact with acetophenone, and that the constitution of the product would indicate whether the carboxyl or the hydroxyl group of the benzoin is the point attacked. A body melting at $122^\circ-124^\circ$ was indeed formed, but the yield was too small to permit of further investigation. The other pairs from the lists given above, when any action occurred, failed likewise to furnish products in quantities sufficient for examination.

Syntheses by Fusion with Small Quantities of Potassium Cyanide or Potassium Hydrate.

It was found that fusion, without solvent, of the materials, in presence of powdered potassium cyanide or hydrate, frequently gave excellent yields of the same substances as were obtained by the usual method. The interaction did not start, as a rule, until 150° was reached. At this temperature the action was frequently violent, water vapor, when formed by the action, being given off rapidly.

Benzaldehyde was heated alone to 150° , a little powdered potassium cyanide was added, and the whole was stirred at intervals for forty-five minutes. After remaining over night the residue became solid and gave a good yield of benzoin. Potassium hydroxide gave no benzoin by this method.

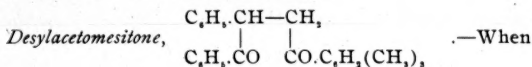
Desylacetophenone was prepared by heating molecular proportions of benzoin and acetophenone with a little powdered potassium cyanide at 150° for twenty minutes. Water vapor was given off vigorously. The mass became solid when cold. The yield was 50 per cent of the theoretical. When potassium hydroxide was used in place of the cyanide the same yield was obtained.

The method of boiling the materials in diluted alcohol, as I originally described it,¹ gives a high-melting by-product not formed here, and the yield is only 38 per cent.

Desyl- α -acetophenone was easily made by heating molec-

¹ J. Chem. Soc., 57, 644.

ular quantities of the constituents at 150° , adding a little powdered potassium hydroxide and stirring during fifteen minutes. Water vapor was given off. When the action had ceased and the mass had cooled the solid residue was rubbed repeatedly with cold alcohol and finally recrystallized from benzene. The yield (58 per cent of the theoretical) was better than by the method described above.



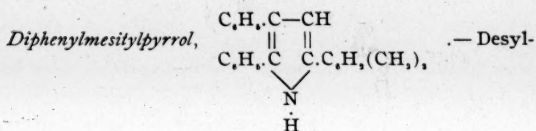
acetomesitone was boiled with benzoin and a little potassium cyanide in 50 per cent alcohol, most of the material was recovered unchanged. The same result was observed on heating in a sealed tube at 100° . On the other hand, when molecular proportions of the two substances were heated at 150° and powdered potassium hydroxide was added, in small portions at a time, vigorous action took place and water vapor was given off. The action ceased after twenty minutes. The product, after rubbing with cold alcohol, was almost perfectly pure. The yield was 61 per cent of the theoretical. After recrystallization from alcohol it formed white needles which melted at 115° .

0.1422 gram substance gave 0.4384 gram CO_2 , and 0.0907 gram H_2O .

	Calculated for $\text{C}_{21}\text{H}_{24}\text{O}_2$	Found.
C	84.26	84.08
H	6.74	7.09

The substance was soluble in 4.5 parts of boiling alcohol, easily soluble in cold benzene and soluble in boiling petroleum ether (b. p. 40° – 60°) from which it crystallized on cooling.

The corresponding diphenylmesitylfurfuran was made by dissolving the ketone in concentrated sulphuric acid, allowing the solution to remain for twenty minutes and pouring the mixture into water. Recrystallized from methyl alcohol, the product formed stellate groups of needles (m. p. 87°). It was soluble in cold petroleum ether.



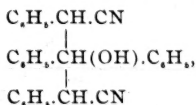
acetomesitone was heated with ammoniacal alcohol in a sealed tube for seven hours at 230° – 240° . When the alcohol had been partly distilled off the residue gave white needles melting at 188° .

0.2218 gram substance gave 8.5 cc. N over 30 per cent KOH at $21^\circ.5$ and 739 mm. (corr.).

	Calculated for $\text{C}_{20}\text{H}_{21}\text{N}$.	Found.
N	4.15	4.25

Action of Potassium Cyanide on a Fused Mixture of Benzyl Cyanide and Benzoin.

When these substances are boiled with diluted alcohol, the simple condensation that might be expected does not take place. Schleussner,¹ working under the direction of Knoevenagel, found that 2 molecules of benzyl cyanide united with 1 of benzoin, with elimination of 1 molecule of water, to form



which was the only product.

Heating the substances in equimolecular proportions without solvent and adding powdered potassium cyanide was equally unsuccessful. Instead of a simple condensation-product, four different substances were formed: (1) Schleussner's body mentioned above (m. p. 181°). (2) A body melting at 86° , which was found to be benzalbenzyl cyanide² (α -phenylcinnamic nitrile). For the purpose of identification, this was converted into the dibromo-addition-product, which was found to melt at 149° – 150° . As Meyer and Frost give the

¹ Inaugural Dissertation; Frankfurt, 1893, p. 11.

² V. Meyer and Frost: Ann. Chem. (Liebig), 250, 157.

melting-point of the latter 129° – 130° (probably a misprint), the nitrile and bromo-derivative were made according to their directions. The agreement in physical properties was complete. (3) A small amount of a yellow amorphous substance not investigated. (4) A substance melting at 227° .5, which was shown by physical properties, nitrogen estimation, and comparison with a sample made in another way, to be diphenylsuccinic nitrile. The melting-point is that of all specimens of the α -form which are not entirely free from the β -variety.

I. 0.1890 gram substance gave 20.6 cc. N over 30 per cent KOH at 19° and 745.5 mm. (corr.).

II. 0.1372 gram substance gave 15 cc. N over 30 per cent KOH at 20° and 743.5 mm. (corr.).

N	Calculated for $C_{18}H_{15}N_3$.	Found.	
		I.	II.
	12.07	12.30	12.25

In conclusion, I wish to thank Dr. H. N. McCoy for the able assistance he has rendered in connection with the experimental work described in this paper.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XVI.—CAMPHORIC ACID.

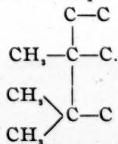
[SEVENTH PAPER.]

BY WILLIAM A. NOYES.

The synthesis of the inactive camphoronic acid by W. H. Perkin,¹ Jr., demonstrating that it is trimethyltricarballic

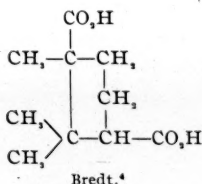
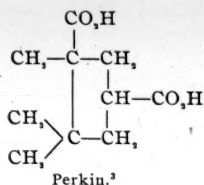
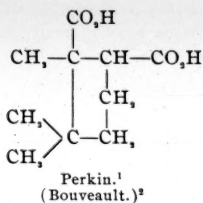
acid, $\begin{array}{c} \text{CH}_3-\text{CO}_2\text{H} \\ | \\ \text{C}(\text{CH}_3)-\text{CO}_2\text{H} \end{array}$, has established almost beyond ques-

$\begin{array}{c} | \\ \text{C}(\text{CH}_3)-\text{CO}_2\text{H} \end{array}$
tion that camphoric acid and camphor must contain the complex



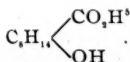
¹ Perkin and Thorpe: J. Chem. Soc., 71, 1169 (1897).

Three formulæ for camphoric acid contain this complex. These are :



In the first of these formulæ camphoric acid is represented as a derivative of succinic acid, in the other two as a derivative of glutaric acid. The following facts appear to the writer inconsistent with the second and third formulæ.

β -Camphoramidic acid, C_8H_{11} , $\begin{array}{l} \text{CO}_2\text{H} \\ \diagdown \\ \text{CONH}_2 \end{array}$, is converted by sodium hypobromite into dihydroaminocampholytic acid. The latter, on treatment with nitrous acid, gives campholytic acid, $\text{C}_8\text{H}_{11}\text{CO}_2\text{H}$, and dihydrohydroxycampholytic acid,



The hydroxyl group of this acid evidently corresponds in position to one of the carboxyl groups of camphoric acid, and must occupy either the β - or γ -position with reference to the carboxyl of the acid. But both campholytic acid and the

¹ Proc. Chem. Soc., 1896, 191.

² Chem. Ztg., 21, 761 (1897).

³ J. Chem. Soc., 73, 798, 806 (1898).

⁴ Ber. d. chem. Ges., 26, 3049 (1893).

⁵ This JOURNAL, 17, 424.

hydroxy acid pass over into ciscampholytic acid¹ on treatment with dilute sulphuric acid. If the hydroxyl group were in the γ -position with reference to the carboxyl it is very difficult to see why a lactone should not be formed under these conditions, as lactones are readily formed in the camphor series. α -Camphoramidic acid gives with sodium hypo-

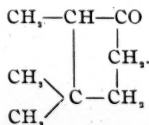
bromite aminolauroic acid, C_8H_{11} , $\begin{matrix} \text{CO}_2\text{H} \\ \diagup \\ \text{NH}_2 \end{matrix}$. The ethyl ester

of the latter gives with nitrous acid the esters of γ -lauronic acid, C_8H_{11} , $\begin{matrix} \text{CO}_2\text{H} \\ \diagup \\ \text{OH} \end{matrix}$, and hydroxylauronic acid, C_8H_{11} , $\begin{matrix} \text{CO}_2\text{H} \\ \diagup \\ \text{OH} \end{matrix}$.

Hydroxylauronic acid, also, does not pass readily into a lactone, although two lactones³ are known which must contain the same carboxyl as that in this acid. Further, on treatment with potassium pyrochromate and sulphuric acid, hydroxylauronic acid loses carbon dioxide and gives a ketone. This points very strongly to the β -position for the hydroxyl group.

Entirely independent evidence of the incorrectness of Perkin's second formula will be given in the latter part of this paper.

Some time ago Mr. E. B. Harris and myself obtained a very small amount of a ketone, $C_8H_{14}O$.⁴ Recently Mr. J. W. Shepherd and myself have prepared the ketone again, by a different method, and have studied some of its derivatives. If the reasoning given above is correct, this ketone is 2,3,3-trimethylcyclopentanone,



The synthesis of this ketone has acquired, therefore, especial interest. While the synthesis has not yet been effected,

¹ The isolauroic acid of Koenigs and Hoerlin. See *This JOURNAL*, 32, 4.

² *This JOURNAL*, 18, 687.

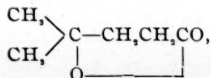
³ Fittig and Woringen: *Ann. Chem. (Liebig)*, 237, 10; Noyes: *This JOURNAL*, 17, 432.

⁴ *This JOURNAL*, 18, 694.

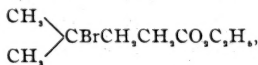
the preliminary work is far enough advanced so that its preparation can be considered as reasonably certain. As the material required is not very easily accessible and the completion of the synthesis may take some time, it seems desirable to give an account of the work which has already been accomplished.

Amyl bromide, from the amyl alcohol of fusel oil and phosphorus tribromide, was converted into the cyanide and into

isocaproic acid, $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} \text{>CH-CH}_2\text{CH}_2\text{CO}_2\text{H}$, by the usual reactions. From the latter isocaprolactone,



was prepared by oxidation in alkaline solution with potassium permanganate.¹ The methods used in separating the lactone would remove any acids formed from other alcohols than isoamyl alcohol, which might be present in the fusel oil. The ethyl ester of γ -bromisocaproic acid,

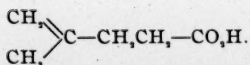


was prepared by treating the isocaprolactone with alcohol and hydrobromic acid.²

1.97 grams (1 atom) of sodium was dissolved in 25 cc. of absolute alcohol and 11 grams (cal. 9.7 g. for 1 mol.) of cyanacetic acid were added to the cooled solution. 19.1 grams (1 mol.) of the γ -bromisocaproic ester were then added and the whole was boiled on the water-bath with a reversed condenser for one and a half to two hours. After cooling, the mixture was treated with water and a few drops of sulphuric acid, the products formed were separated from the aqueous solution, and the latter was extracted two or three times with ether. It was found that the brom-ester had been mostly decomposed with the formation of the ester of an unsaturated acid, probably Δ^1 -methyl-(2)-pentenoic(5) acid,

¹ Bredt : Ann. Chem. (Liebig), 208, 55.

² Bredt : Ber. d. chem. Ges., 19, 514.



After distilling this ester and the unchanged cyanacetic ester under diminished pressure, however, a residue remained which mostly solidified on cooling. This residue yielded, on crystallization from alcohol, a little less than 2 grams of a pure substance.

Dimethylcyanocarboxethylcyclopentanone,

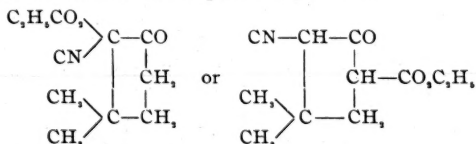
$\text{C}_9\text{H}_{15}\text{O}(\text{CH}_3)_2\text{CN}.\text{CO}_2\text{C}_2\text{H}_5$, obtained in this manner, crystallizes from alcohol in colorless needles, which melt at $148^\circ.5$. It is rather difficultly soluble in alcohol, almost insoluble in water. It gives no color with ferric chloride.

I. 0.2042 gram of the substance gave 0.1343 gram H_2O , and 0.4726 gram CO_2 .

II. 0.994 gram of the substance gave 7.52 cc. of nitrogen at $20^\circ.5$ and 585 mm.

	Calculated for $\text{C}_{11}\text{H}_{15}\text{NO}_3$.	Found.	
		I.	II.
C_{11}	63.16	63.12	
H_{15}	7.18	7.31	
N	6.70		6.80

The structure of the compound may be either



It will probably be possible to decide between these formulæ by the use of the methyl ester of the γ -bromisocaproic acid instead of the ethyl ester. When the substance is heated with water in a sealed tube at 150° – 160° for two or three hours the cyanogen group is saponified and eliminated. That the resulting oil is nearly free from nitrogen and that its boiling-point and composition agree approximately with those to be expected for dimethylcarboxethylcyclopentanone has been demonstrated, but the body has not been prepared in pure condition.

By the use of acetoacetic ester in place of the cyanacetic ester, as above, a small amount of an oil boiling at 180° – 190° under a pressure of 30 mm. was obtained. Also with methyl malonic ester an oil boiling at 195° – 210° (30 mm.) was formed. The yields are in both cases only about 10 per cent of the weight of the brom-ester employed. The use of sodium methyl malonic ester in suspension in benzene did not give a better yield.

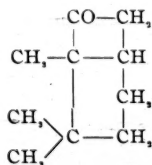
It seems probable that from some one of these compounds it will be possible to prepare the trimethylcyclopentanone which is desired.

Some time ago¹ I established the following genetic relationship: α -camphoramidic acid $\rightarrow$ aminolauronic acid $\rightarrow$ γ -lauronic acid $\rightarrow$ campholactone. Claisen and Manasse² have

shown that isonitrosocamphor, C_8H_{11} , $\begin{matrix} & C=NOH \\ & | \\ CH_3-C & \\ & | \\ & CO \end{matrix}$, on treat-

ment with hydrochloric acid, passes over into a α -camphoramidic acid. This demonstrates that the carbonyl of camphor corresponds to the carboxyl of aminolauronic acid.

I have also shown³ that the carboxyl of aminolauronic acid is tertiary while that of dihydroaminocampholytic acid is secondary. If we assume that camphoric acid is a derivative of succinic acid, the formula for camphor which follows is:



This formula was first proposed by Bouveault,⁴ though the corresponding formula for camphoric acid had been previously proposed by Perkin (see above). By an unfortunate error the relative positions of the carbonyl and methylene groups

¹ This JOURNAL, 17, 425.

² Ann. Chem. (Liebig), 274, 71; This JOURNAL, 16, 507.

³ This JOURNAL, 18, 686.

⁴ Chem. Ztg., 21, 761.

are interchanged in the abstract of Bouveault's paper in the *Centralblatt*, (1897, II, 855).

α -HYDROXYDIHYDROCISCAMPHOLYTIC ACID.

WITH J. W. SHEPHERD.

The ciscampholytic acid required for the preparation of this acid was prepared by the method of Blanc,¹ slightly modified. 25 grams of camphoric anhydride were dissolved in 100 cc. of dry chloroform, slightly warmed; the solution was filtered if not clear; 23 grams of aluminium chloride were added in portions of 4 to 5 grams during a period of five to ten minutes. If the solution warmed at first, the flask was placed in cold water, but very soon the evolution of carbon monoxide became rapid and the solution cooled spontaneously. In order to follow the course of the reaction, the flask was closed with a stopper bearing a delivery tube, and the gas evolved was collected in a large flask over water. When about 4 liters, somewhat more than the theory because of vapor of chloroform, had been collected, and the evolution of the gas had nearly ceased, the chloroform solution was poured into 700 cc. of ice-water, some hydrochloric acid was added, and the aqueous solution was separated and discarded. After washing the chloroform solution a couple of times with water containing hydrochloric acid, an excess of a strong solution of sodium hydroxide was added, and the chloroform was distilled off in a current of steam. After cooling the alkaline solution, the impure ciscampholytic acid was precipitated with hydrochloric acid, filtered off, washed, and dried. Instead of purifying the acid by crystallization or by distilling with steam as recommended by Blanc, it was found much quicker and better to distil it under diminished pressure, using a distilling-bulb to which a wide side-tube was sealed to collect the solid acid. The acid was distilled under a pressure of 30-50 mm., with the oil-bath in which the bulb was heated at about 190°. One distillation gave a pure acid. 150 grams of camphoric anhydride worked up in 6 portions, as described, gave 92 grams of ciscampholytic acid, or 73 per cent of the theoretical yield.

¹ Bull. Soc. Chim. [III], 15, 1191. See also Perkin: Jour. Chem. Soc. (London), 73, 801, 828 (1898).

The ciscampholytic acid was converted into the dihydro acid by reduction with amyl alcohol and sodium.¹ The dihydro acid was converted into the chloride of the α -brom acid by treatment with phosphorus pentachloride and bromine. After distilling away most of the phosphorus oxychloride under diminished pressure, the résidue was poured into an excess of absolute alcohol, and the mixture allowed to stand over night. The ester of the α -brom acid was then precipitated by the addition of water.

Thirty grams of the ester were put in a 500 cc. glass-stoppered bottle, with 40-50 grams of crystallized barium hydroxide and 400 cc. of water. Most of the air in the bottle was removed by connecting the lip of the bottle with a wide glass tube by means of rubber tubing, the stopper of the bottle being left loose in the neck. After exhaustion the stopper, which was smeared with a stop-cock lubricant, was jarred into place and the glass tube removed. The removal of the air prevented pressure within the bottle on heating, and also caused a much more thorough mixing of the contents on shaking. The bottle was attached to the fly wheel of a small hot-air motor and shaken continuously for several days. It was also warmed to 30°-40° by placing under it a piece of sheet-iron heated with a Bunsen burner. It is hardly necessary to add that many other methods were tried for the preparation of the hydroxy acid before this one was finally devised.

Even under the conditions described, most of the ester is converted back into ciscampholytic acid. Only about 10 per cent is transformed into the hydroxy acid.

After filtering from unchanged ester the solution was acidified and the precipitated ciscampholytic acid was filtered off at once. The hydroxy acid passed, mostly, into the filtrate and was obtained by repeated extractions with ether. From the precipitated ciscampholytic acid a small amount of the hydroxy acid could be separated by dissolving in the theoretical amount of sodium hydroxide, adding hydrochloric acid for partial precipitation, and distilling away the ciscampholytic acid with steam. Probably the distillation of the ammonium salts with steam would have been better.² The hy-

¹ This JOURNAL, 18, 689 (1896); Perkin: J. Chem. Soc., 73, 836 (1898).

² Perkin: J. Chem. Soc., 73, 830.

droxy acid was purified by crystallization from ligroin or benzene.

α-Hydroxydihydrociscampholytic Acid, $C_7H_{14}O_3$, $\begin{matrix} \text{CO}_2\text{H} \\ \diagup \\ \text{C}_7\text{H}_{11} \\ \diagdown \\ \text{OH} \end{matrix}$, crys-

tallizes in needles which melt at 112° . It is difficultly soluble in water and in ligroin, somewhat more easily soluble in benzene.

I. 0.2462 gram substance gave 0.2038 gram H_2O , and 0.5600 gram CO_2 .

II. 0.1562 gram substance gave 0.1311 gram H_2O , and 0.3600 gram CO_2 .

	Calculated for $C_7H_{14}O_3$	Found.	
		I.	II.
C	62.79	62.03	62.85
H	9.30	9.20	9.32

Ketone, $C_7H_{12}O$.—This ketone¹ was prepared by distilling the hydroxy acid with lead peroxide and dilute sulphuric acid. 1 gram of the acid, 2 grams of lead peroxide, 4 cc. of dilute sulphuric acid, and 45 cc. of water were put in a distilling bulb, and the mixture distilled very slowly as long as oily drops of the ketone appeared in the distillate. The water was separated from the ketone, the former was returned to the distilling-bulb, more of the acid, lead peroxide, and sulphuric acid were added, and the distillation was continued. 2.5 grams of the acid gave, in this way, about 1 gram of the ketone. In working with larger amounts the yield could probably be increased. The ketone was dried with potassium carbonate and distilled. It boils at 167° – 169° and has a specific gravity of 0.8956^{20}_4 or 0.8911^{25}_4 . These constants cannot be considered very accurate, as they were determined with a very small amount of the ketone. They are of especial interest for comparison with 3,5-dimethylcyclohexanone, which boils at 181° – 182° and has a specific gravity of 0.8994^{17}_4 .² The lower boiling-point and specific gravity of the ketone from camphor indicate very clearly that it is a derivative of cyclopentanone.

The ketone has a strong odor like that of peppermint and at

¹ This JOURNAL, 18, 694.

² Knoevenagel: Ann. Chem. (Liebig), 297, 164.

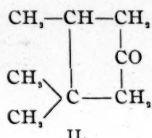
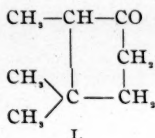
the same time a musty odor. It is nearly insoluble in water.

The *oxime*,¹ $C_8H_{11}NOH$, was prepared by adding a strong solution of hydroxylamine chloride and sodium hydroxide to an alcoholic solution of the ketone. It crystallizes from dilute alcohol in needles which melt at 104° . Its odor resembles that of camphoroxime.

0.1005 gram gave 10.72 cc. of nitrogen at 17° and 634 mm.

	Calculated for $C_8H_{11}NOH$.	Found.
N	9.93	10.17

If Perkin's (Bouveault's) first formula for camphoric acid is correct, the ketone must have the structure designated I below. If the formula at present advocated by Perkin is true, the ketone must have the structure designated II.



A ketone of structure I would condense with 1 molecule of benzaldehyde; one of structure II would condense with 2 molecules.

0.286 gram of the ketone, 0.5 gram of benzaldehyde (2 mols.), 3 cc. of alcohol, and 0.5 cc. of sodium hydroxide (10 per cent) were mixed and allowed to stand over night. There was a slight rise in temperature at first and the reaction was probably complete in a few minutes, and appears to be quantitative. The condensation-product was precipitated with water and taken up with ether. After distilling away the ether, the excess of benzaldehyde was distilled under a pressure of 20-30 mm., the bulb being heated in an oil-bath to 185° . The residue solidified on cooling and weighed 0.393 gram. The theory for a compound formed by condensation with 1 molecule of benzaldehyde is 0.477 gram; with 2 molecules, 0.685 gram. The compound crystallizes from alcohol in needles which melt at 74° . It is difficultly soluble in alcohol, almost insoluble in water.

¹ This JOURNAL, 18, 694; 20, 789.

0.1227 gram substance gave 0.0935 gram H_2O , and 0.3758 gram CO_2 .

	Calculated for $C_8H_{11}O=CHC_6H_5$, $C_8H_5CH=C_6H_5O=CHC_6H_5$.		Found.
C	84.11	87.41	83.54
H	8.41	7.28	8.47

The ketone condenses, therefore, with only 1 molecule of benzaldehyde and Perkin's second formula for camphoric acid is, apparently, excluded. These results are consistent with either the first formula of Perkin (Bouveault), or with Bredt's formula. For the reasons given above the former formula appears to the writer more probable.

One-half gram of the ketone was submitted to oxidation with potassium pyrochromate and sulphuric acid, but owing to the small amount of material available, no definite results have been obtained.

Contributions from the Sheffield Laboratory of Yale University.

LXXII.—RESEARCHES ON SUBSTITUTION: THE ACTION OF BROMINE ON METACHLOR-, METABROM-, AND METAIODANILINES.

[SECOND PAPER.]

BY H. L. WHEELER AND WILLIAM VALENTINE.

The action of metasubstituted anilines with chlorine and bromine has been thoroughly investigated only in regard to their behavior on saturation. In each case examined it has been found that the halogens enter the 2, 4, and 6 positions, the meta derivatives behaving, in this respect, precisely like aniline.

With this fact at hand, Langer¹ published the following law: "Dass bei weiterer Substitution des Anilins solche Substituenten, die zur Amido-gruppe die Metastellung einnehmen, gar keinen bemerkbaren Einfluss ausüben und die Zahl der neu eintretenden Halogenatome nicht verringern."

Previously Nölting,² in calling attention to this similarity in behavior stated: "Ueberhaupt verhält sich ein bei 3 substituirtes Anilin Agentien gegenüber gerade so wie ein gar nicht substituirtes."

¹ Ann. Chem. (Liebig), 215, 107.

² Ber. d. chem. Ges., 8, 1093.

These statements are perfectly true when applied in the sense indicated above, but it appears that, with the exception mentioned below, no attempts have been made to determine what the first product is, or what the chief products are when the free anilines are subjected to less energetic treatment.¹ Consequently it has not been shown in what order the different positions 2, 4, and 6 are substituted, and whether or not in these intermediate stages any influence of the substituent in the meta position is to be observed.

Owing to the energy with which the aromatic amines are attacked by chlorine and bromine, and also on account of the formation of by-products, it is customary to moderate the action by employing the acetyl derivatives instead of the free bases. It has been assumed that this procedure simply protects the amino group or moderates the violence of the reaction. Whether in the case of meta substituted anilines it exerts any other influence in the further substitution than this has not been determined, except in the instance described below. In the cases where the acetyl derivatives have been employed it has been found that the substitution takes place smoothly, the halogen entering the position para to the amino group and practically without the formation of by-products. In order to obtain the higher bromine substitution-products the free bases are employed, as, otherwise, the bromination is frequently arrested with the formation of the monobrom derivative, the next step being the formation of perhalides.²

Since the question whether a substituent in the meta position influences the further substitution of the aniline had been examined from only one side, one of us investigated the behavior of metanitrilaniline³ with bromine, in glacial acetic acid, and found that the nitro group in the meta position exerts not only a protective or retarding influence⁴ but also a directing influence on the substitution. The chief product formed was the sweet-tasting 6-brom-3-nitrilaniline and not the expected

¹ Beilstein and Kurbatow thoroughly investigated the action of chlorine on metachloracetanilide (*Ann. Chem. (Liebig)*, 196, 215), but do not mention the action of the free base.

² Wheeler and Walden: *This JOURNAL*, 18, 25; Wheeler, Barnes, and Pratt: *Ibid.*, 19, 672.

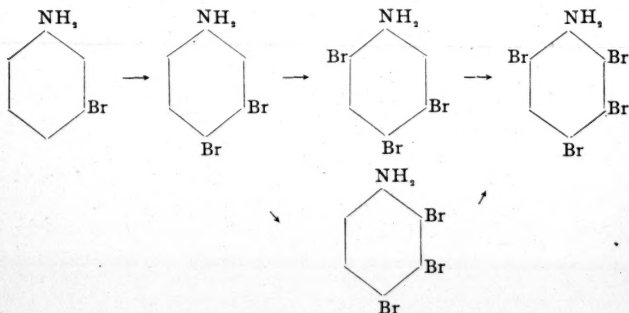
³ *This JOURNAL*, 17, 697.

⁴ A fact previously noticed by Michael and Norton (*Ber. d. chem. Ges.*, 11, 112), in the case of substitution by iodine monochloride.

4-brom-3-nitraniline, which should result from analogy, or if the nitro group exerted no influence. Moreover, it was found that acetylmetanitrilaniline gave, as the chief product, a different mono derivative, 4-brom-3-nitraniline, than the free base.

We have now extended the examination of meta substituted anilines, and, in this paper, we describe the results of our experiments on the influence exerted when the meta substituent is a halogen, the bromination being conducted as before in a glacial acetic acid solution.¹

Now, it might be expected that *m*-chlor-, *m*-brom-, and *m*-iodanilines would behave with bromine under similar conditions, like *m*-nitraniline. This, however, is not the case. The chief products formed in the case of the *m*-halogen anilines have been found to be the para derivatives. For example, in the case of *m*-bromaniline (43 grams with 1 molecular proportion of bromine) the product obtained in largest amount was 3,4-dibromaniline (26 grams); next in amount was a mixture of 3,4,6-tribromaniline (in larger amount) with 2,3,4-tribromaniline; then followed 2,3,4,6-tetrabromaniline, from which it follows that the relative tendency of bromine to substitute the hydrogen atoms in these compounds may be expressed in the terms $4 > 6 > 2$, the course of the reaction proceeding as follows:



¹ Glacial acetic acid has proved in each case to be well suited for the examination of the lower brominated products. It not only moderates the action less than the acetyl compounds, permitting the examination of the behavior of the free bases, but also simplifies the purification of the products.

The bromination of metachlor- and metaiodaniline gave similar results, the bromine entering the para position to the amino group and forming chiefly a monobrom derivative.

Each of these cases is therefore an exception to the rule of Kehrmann,¹ *i. e.*, that the entering substituent generally takes the ortho position to the substituent of least molecular magnitude.

From the above it is seen that the nitro group in the meta position exerts a different directing influence on the further substitution by bromine than that exerted by the halogens; that the course of the reaction or the energy with which bromination occurs is in opposite directions around the molecules previous to the formation of the final 2,4,6-derivative.

It is well known that the nitro group in nitrobenzene exerts a different directing influence on further substitution from that exerted by the halogens in chlor-, brom-, and iodbenzene. Further substitution in the first case leads to the formation of meta derivatives, while in the latter ortho and para compounds result. The groups, atoms, or radicals that influence the entering substituent to take the ortho or para position have been termed by Lellmann² substituents of the *first class*. To this class belong the halogens, the alkyl radicals, and the groups $-\text{NH}_2$, $-\text{OH}$, $-\text{CH}_2\text{R}$, while the groups $-\text{NO}_2$, $-\text{CO}_2\text{H}$, $-\text{SO}_3\text{H}$, etc., which yield meta derivatives on further substitution are known as substituents of the *second class*.

It is suggested by our work so far that a difference in directing influence is still retained by these radicals in the meta-substituted anilines. That, in general, meta-substituted anilines containing substituents of Lellmann's first class will be found to give chiefly a 4-halogen derivative while, on the other hand, those with the radicals of the second class, like metanitriline, will give a 6-halogen compound as the chief product. We intend to continue the investigation of the influence exerted on the substitution of anilines by groups in the meta position, and we hope, later, to decide the above simple questions which, however, involve considerable work.

¹ Ber. d. chem. Ges., **23**, 130.

² Principien d. Org. Synthese, p. 11.

The Bromination of m-Chloraniline.

When 50 grams of metachloraniline were dissolved in 400 cc. of glacial acetic acid and treated with 62.7 grams of bromine (1 molecule) in the form of vapor, by means of a stream of dry air, a colorless crystalline precipitate separated. This, when dried, weighed 85 grams (Precipitate *A*). It consisted mostly of the mono- and dibrom derivatives in the form of hydrobromic acid salts.¹ The monobrom derivative was extracted by treating this mixture repeatedly with water (Solution *B*), and, on precipitating with ammonia, 35 grams of crude material were obtained.²

The treatment with water left the di- and a small amount of tribrom derivatives undissolved, weight 23 grams (Residue *C*). The glacial acetic acid (Solution *A*) was diluted with about three or four times its volume of water, which resulted in the precipitation of the rest of the tribrom derivative³ (1 gram) in practically pure condition (Precipitate *D*).

The dilute acetic acid solution was then precipitated with strong ammonia, when the unaltered metachloraniline with some monobrom derivative was obtained (Precipitate *E*). The method of examining and purifying these crude products is given below under their separate heads.

The following calculation, being a check on the above weights, confirms the analytical results and the chemical behavior of the products :

	Bromine. Grams.
<i>B</i> 35 grams of monobrom derivative account for	27.1
<i>C</i> 23 " " dibrom " " "	25.8
<i>D</i> 1 gram " tribrom " accounts "	1.3
Total	54.2

That 8.5 grams of bromine are apparently not accounted for is due to the fact that the monobrom derivative mixed with unaltered *m*-chloraniline (Precipitate *E*) is not included in the above calculation, and also to the fact that the above are

¹ It also contained the hydrobromic acid salt of unaltered material.

² A loss occurs here owing to the solubility of the material in the solutions precipitated by ammonia. As this appeared to be chiefly unaltered material it was not recovered.

³ Some loss is to be expected here owing to the volume of the solutions.

weights of crude products and not of perfectly pure material.

It is to be expected that the loss in the case of metachloraniline would be greater than with metabromaniline since the chlorine compounds are more soluble. This has been found to be the case, so that the solubility explains a part of this loss. The amount of bromine lost by action on the glacial acetic acid is probably very small. Each one of the brominations described in this paper has been repeated and the results confirmed.

3-Chlor-4-bromaniline.—The precipitate produced by ammonia in Solution *B* was crystallized from dilute alcohol, when four- and six-sided colorless plates separated. They melted constantly from 67° – 68° , and a determination of the halogens shows that this material is a monobrom derivative :

	Calculated for C_6H_4NCIBr .	Found.
Cl	17.2	17.2
Br	38.7	38.2

The structure is shown by the fact that it gives orthochlorbrombenzene with ethyl nitrite, and since it is formed almost quantitatively by brominating acetyl-*m*-chloraniline, the bromine as usual taking the position para to the acetyl group.

The *hydrochloride*, prepared by passing hydrochloric acid gas into the alcoholic solution of the base, crystallizes in colorless needles. A hydrochloric acid determination gave :

	Calculated for $C_6H_4NCIBr.HCl$.	Found.
HCl	15.0	14.6

It is readily soluble in water, less readily in alcohol, and insoluble in benzene. It blackens when heated to about 210° .

The *sulphate* is obtained in the form of colorless plates when the base is treated with dilute sulphuric acid. A sulphuric acid determination gave :

	Calculated for $(C_6H_4NCIBr)_2.H_2SO_4$.	Found.
H_2SO_4	19.2	19.5

The *picrate* is obtained as a precipitate by adding an alcoholic solution of picric acid to a solution of the base. It crys-

tallizes in yellow needles which melt at 141° . A nitrogen determination gave the following result:

N	Calculated for $C_6H_5NClBr \cdot C_6H_5N_2O_7$	Found.
	12.9	12.7

1,2-Chlorbrombenzene.—Six grams of the precipitate produced by ammonia in Solution *B* were treated with an excess of ethyl nitrite in the presence of a little concentrated hydrochloric acid. After warming, the material was taken up in ether, washed, dried, and distilled, when 4.5 grams of colorless oil were obtained, boiling from 200° – 210° . On redistilling at 772 mm. pressure it all boiled from 201° – 204° . It refused to solidify. *p*-Chlorbrombenzene is a solid melting at 67.4° , while the boiling-points of ortho-, meta-, and parachlorbrombenzene are given by Dobbie and Marsden¹ as 204° , 196° , and 196.3° , respectively. Our material is therefore orthochlorbrombenzene.

Nitration of 1,2-Chlorbrombenzene.—In order further to characterize orthochlorbrombenzene we have examined its behavior towards nitric acid. 2 to 3 grams of orthochlorbrombenzene were dissolved in fuming nitric acid and warmed. Water was then added, and the precipitated material, crystallized from 75 per cent alcohol, gave colorless needles melting from 49° – 50° . Three crystallizations did not alter the melting-point.² A nitrogen determination gave:

N	Calculated for $C_6H_5NO_2ClBr$	Found.
	5.9	6.3

The structure $C_6H_5NO_2ClBr$, 1,4,3, is assigned to this compound, because on reduction it did not give 3-chlor-4-bromaniline, melting at 67° , but a base melting at 75° , after repeated crystallizations. Since, in general, the tendency of ortho compounds, on nitration, is to form an unsymmetrical in preference to a vicinal derivative, it follows that this is in all probability *4-chlor-3-bromaniline*. It was not further examined.

¹ J. Chem. Soc., 1898, 255.

² The true melting-point of 3-brom-4-chlornitrobenzene is probably 60° , the above material being mixed with some 3-chlor-4-bromnitrobenzene.

3-Chlor-4-brom-2,6-dinitraniline.—Eight grams of 3-chlor-4-bromaniline were heated on the steam-bath with concentrated nitric acid. In a few minutes reaction set in with evolution of red fumes. After this was over the solution was diluted with water and the precipitate crystallized from absolute alcohol, in which it is difficultly soluble, when it was obtained in the form of dark-yellow prisms, melting from 169°–170°. A nitrogen determination gave:

	Calculated for $C_6H_3N_2O_4ClBr$.	Found.
N	14.2	14.7

3-Chlor-4-bromacetanilide.—Fifty grams of metachloracetanilide were dissolved in glacial acetic acid, the calculated quantity of bromine was added, and the mixture allowed to stand a few minutes. Water was then added, and the precipitate was crystallized from 50 per cent acetic acid, when it was found to melt sharply at 125°; yield 70 grams, calculated 73 grams. A nitrogen determination gave:

	Calculated for $C_8H_7NOClBr$.	Found.
N	5.6	5.7

The acetyl group is easily removed from this by boiling the alcoholic solution with a little concentrated hydrochloric acid. This gives the hydrochloride of a base which latter is identical in every respect with the monobrom compound formed on brominating *m*-chloraniline.

3-Chlor-4-brom-6-nitroacetanilide.—One part of 3-chlor-4-bromacetanilide is dissolved in 3 parts of cold nitric acid (sp. gr. 1.52) and the solution is allowed to stand for a few minutes. It is then poured into ice-water, and the precipitate, crystallized from absolute alcohol, gives colorless, flattened prisms or plates. These melt from 129°–130°. Yield 7 grams from 5 grams acetyl compound. A nitrogen determination gave:

	Calculated for $C_8H_4N_2O_5ClBr$.	Found.
N	9.5	9.3

3-Chlor-4-brom-6-nitraniline.—Five grams of the above substance were boiled with alcohol containing some concentrated hydrochloric acid when crystalline material began to sepa-

rate. Water then precipitated the base completely, ammonia giving no precipitate in the filtrate, as the substance is too weakly basic to form a salt under these conditions. It crystallizes from alcohol in long yellow needle-like prisms which melt from 202° – 203° . A nitrogen determination gave:

	Calculated for $C_8H_4N_2O_3ClBr$.	Found.
N	11.1	11.0

4-Chlor-3-bromnitrobenzene.—From 2 to 3 grams of the above compound were treated with nitrous acid in alcohol. The material after this treatment was crystallized from alcohol, when light-yellow needles melting at 60° were obtained.

4-Chlor-3-bromaniline.—On reducing the above 4-chlor-3-bromnitrobenzene with tin and hydrochloric acid, a product identical with the base obtained from the nitration of 1,2-chlorbrombenzene should result. This being the case, the structure of this and the four preceding compounds is proved. In fact, a base was obtained which appears to be identical with that described under the head of the nitration of 1,2-chlorbrombenzene. The crude product melted at 75° , but on further crystallizing it was obtained in the form of colorless, shining plates, which melted at 78° . A nitrogen determination gave:

	Calculated for C_8H_7NClBr .	Found.
N	6.8	6.5

3-Chlor-4,6-dibromaniline.—Residue *B* (see above), after being treated thoroughly with water, was crystallized from alcohol, when thin, colorless plates were obtained, melting from 79° – 80° . A halogen determination gave:

	Calculated for $C_8H_4NClBr_2$.	Found.
Cl	12.4	12.4
Br	56.0	55.9

3-Chlor-2,4,6-tribromaniline.—On crystallizing Precipitate *C* (see above) from alcohol this compound was obtained. It had all the properties described by Langer.¹

¹ *Loc. cit.*

The Bromination of m-Bromaniline.

In one experiment 43 grams of metabromaniline were dissolved in 350cc. of glacial acetic acid, and 40 grams of bromine (1 molecule) added as described in the previous case. The precipitate produced (*A*) weighed 90 grams. The soluble hydrobromides removed by water and precipitated by ammonia (*B*) weighed 26 grams. The residue (*C*) weighed 16 grams. The precipitate (*D*) produced by water in the glacial acid solution weighed 1 gram, and on filtering from this and adding ammonia practically nothing but unaltered material was found.

The results are checked by the following calculation :

	Bromine. Grams.
<i>B.</i> 26 grams of dibrom derivative account for	17.7
<i>C.</i> 16 " " tribrom " "	15.5
<i>D.</i> 1 gram " tetrabrom " accounts "	1.1
Total	34.3

This gives 5.7 grams of bromine not accounted for. It is to be explained in the same manner as the loss in the case of the previous bromination.

3,4-Dibromaniline.—The precipitate by ammonia (*B*), after two crystallizations from 50 per cent alcohol, melted from 80°–81°. It had all the properties of the base produced by reducing 3,4-dibromnitrobenzene.¹

The *picrate* was obtained by mixing alcoholic solutions of the constituents. The product crystallized from water gave yellow needles, melting at 149°. A nitrogen determination gave :

	Calculated for $C_8H_7NBr_2 \cdot C_6H_5N_3O_7$.	Found.
N	11.66	11.7

The *hydrochloride* crystallizes from dilute hydrochloric acid in colorless prisms which decompose when heated from 220°–230°. A hydrochloric acid determination gave :

	Calculated for $C_8H_7NBr_2 \cdot HCl$.	Found.
HCl	12.7	12.7

¹ Korner : Jahresb., 1875, 311.

The sulphate crystallizes in colorless plates.

	Calculated for (C ₆ H ₃ NBr ₃) ₂ ·H ₂ SO ₄	Found.
H ₂ SO ₄	16.3	16.5

3,4-Dibromacetanilide.—This has recently been prepared¹ by brominating metabromacetanilide. We have prepared it in this way, and also by acetylating precipitate *B*. It crystallizes in slender prisms melting at 128°, as stated by Körner.

3,4,6-Tribromaniline.—When residue *C* (see above) was crystallized from alcohol, colorless needles were obtained which melted from 115°–116°. This proved to be 2,3,4,6-tetrabromaniline. In order to separate this from the tribromanilines the material was taken up in dry ether and hydrochloric acid gas passed in. This produced a precipitate of the hydrochloric acid salts of the tribromanilines, while the tetrabromaniline remained in solution. The precipitate was treated with ammonia and repeatedly crystallized from alcohol, when it melted from 84°–89°; It being still impure it was converted into the acetyl compound. This, on repeated crystallization from alcohol, melted from 188°–189°; on now removing the acetyl group, the free base melted sharply from 85°–86°. A bromine determination in the product melting from 84°–89° gave:

	Calculated for C ₆ H ₃ NBr ₃	Found.
Br	72.7	72.2

1,3,4-Tribromobenzene.—In order to determine the structure of the above tribromaniline, 1 gram was treated with nitrous acid in alcoholic solution, when a small amount of fine, colorless needles were obtained; these melted from 44°–45°, and were undoubtedly 1,3,4-tribromobenzene, which forms needles and melts at 44°. The above base, melting at 85°–86° is, therefore, 3,4,6-tribromaniline.

3,4,6-Tribromacetanilide is therefore the compound crystallizing in colorless needles and melting from 188°–189°, as mentioned above. This same compound and the corresponding base were also prepared in the following manner: *p*-Di-

¹ Körner: Bull. Soc. Chim. (Paris), 1896, 1047.

brombenzene was nitrated and the product reduced; this gave 3,6-dibromaniline, which melted from 51° – 52° , and agreed in properties with Meyer and Stüber's¹ description except that, when sufficiently purified, it does not have the odor of α -naphthylamine. On acetylating, 3,6-dibromacetanilide was obtained.

3,6-Dibromacetanilide, on crystallizing from alcohol, was found to melt from 171° – 172° , and a nitrogen determination gave:

	Calculated for $C_8H_7NOBr_2$.	Found.
N	4.8	4.8

3,4,6-Tribromacetanilide.—The above acetyl compound was dissolved in glacial acetic acid and treated with 1 molecular proportion of bromine, when a product was obtained which crystallized from alcohol in colorless needles and melted from 188° – 189° . This is identical in every respect with the acetyl compound obtained from Residue C. A nitrogen determination gave:

	Calculated for $C_8H_5NOBr_3$.	Found.
N	3.9	3.8

Here again the different influence of groups in the meta position is to be noticed. The above 3,6-dibromacetanilide is readily attacked by bromine, while 3-nitro-6-bromacetanilide can be crystallized unaltered from pure bromine.

1,2,3-Tribrombenzene.—In another experiment the crude product, C, after removal of 2,3,4,6-tetrabrombenzene, was treated directly with nitrous acid, in alcohol, in the presence of hydrochloric acid.² On distilling with steam an oil was obtained which, after solidification and crystallization from alcohol, was obtained in the form of colorless plates. These had the odor of the brombenzenes and melted at 85° . Körner³ gives the melting-point of 1,2,3-tribrombenzene as 87° .4.

It follows, therefore, that the residue C consists of 3,4,6-tribromaniline (isolated), 2,3,4-tribromaniline (not isolated), and 2,3,4,6-tetrabromaniline (isolated).

¹ Ann. Chem. (Liebig), 165, 180.

² These tribromanilines have a great tendency to form orange-colored precipitates (diazamidobenzenes?) which are decomposed with difficulty by nitrous acid.

³ Gazz. chim. ital., 4, 408.

2,3,4,6-Tetrabrombenzene.—The precipitate *D* was found to consist entirely of this. It forms colorless needles, melting from 115°–116°, as described by Körner.¹

The Bromination of m-Iodaniline.

In one experiment 53 grams of *m*-iodaniline were dissolved in 400 cc. of glacial acetic acid, and 39 grams of bromine were added in the form of vapor. This produced a crystalline precipitate weighing 83 grams (*A*). The material obtained by extracting this with water and precipitating with ammonia (Precipitate *B*) weighed 35 grams. The residue *C* weighed 30 grams, and the precipitate *D*, produced by water in the glacial acetic acid solution, weighed 1 gram. Ammonia added to the filtrate from this gave unaltered material. Checking these weights now by the following calculation we find that :

	Bromine. Grams.
<i>B</i> . 35 grams of monobrom derivative account for	18.7
<i>C</i> . 30 " " dibrom " "	25.4
<i>D</i> . 1 gram " tribrom " accounts	1.0
Total	45.1

This gives an excess of 6.1 grams of bromine. The error lies chiefly in the assumption that *B* consists entirely of monobrom derivative. As it was not free from oil, it must have contained unaltered material which, calculated as monobrom derivative, explains this excess.

3-Iod-4-bromaniline.—Precipitate *B* was crystallized from alcohol, when it was obtained in the form of colorless plates, melting at 77°. A bromine and iodine determination gave the following :

	Calculated for C_6H_4NBri .	Found.
Br	26.8	27.3
I	42.6	42.3

We proved the structure of this compound in the following manner: 2.5 grams of 6-brom-3-nitraniline (which gives *p*-bromnitrobenzene with ethyl nitrite) were diazotized and the amino group replaced by iodine by means of potassium

¹ Loc Cit.

iodide. The *3-iod-4-bromnitrobenzene* thus produced crystallized from alcohol in four- and six-sided tables, which melt at 95° – 96° , and on reduction the material gave a base melting at 77° and having all the properties of the compound obtained by brominating *m*-iodaniline.

The *hydrochloride* was made by passing hydrogen chloride into the benzene solution of the base. It crystallizes from alcohol in long, slender, colorless needles, which decompose when heated at about 210° . A determination of the hydrochloric acid gave :

	Calculated for $C_6H_4NBrI.HCl$.	Found.
HCl	10.9	10.6

The *sulphate* crystallizes in colorless plates from dilute sulphuric acid.

	Calculated for $(C_6H_4NBrI)_2.H_2SO_4$.	Found.
H_2SO_4	14.1	14.2

The *picrate* crystallizes from water in yellow needles, which melt from 158° – 159° . A nitrogen determination gave :

	Calculated for $C_6H_4NBrI.C_6H_5N_3O_7$.	Found.
N	10.6	10.9

3-Iod-4-bromacetanilide was prepared by acetylating the above base in the usual way. On crystallizing from alcohol it melted from 138° – 139° . A nitrogen determination gave :

	Calculated for C_8H_7NOBrI .	Found.
N	4.1	4.2

3-Iod-4,6-dibromaniline.—The residue *C*, which was insoluble in water, on repeated crystallizations from alcohol, separated in the form of long, colorless prisms, melting at 81° . A bromine and iodine determination gave :

	Calculated for $C_6H_3NBr_2I$.	Found.
Br	42.4	42.6
I	33.7	33.6

3-Iod-2,4,6-tribromaniline.—The precipitate *D*, produced by adding water to the glacial acetic acid solution, was crystallized from alcohol, when minute colorless prisms or plates

were obtained, melting at 115° – 116° . A bromine and iodine determination gave :

	Calculated for $C_8H_3NBr_3I$.	Found.
Br	52.6	52.3
I	27.8	27.8

NEW HAVEN, CONN., June, 1899.

Contribution from the Department of General Chemistry, University of Michigan.

A SIMPLIFICATION OF BECKMANN'S BOILING-POINT APPARATUS.

By S. L. BIGELOW.

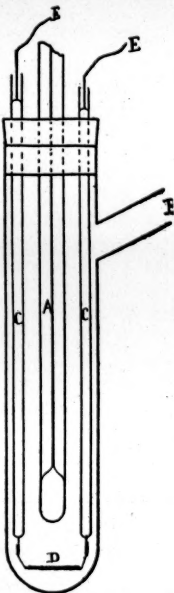
Most of the attachments to Beckmann's boiling-point apparatus, such as the asbestos stove, the outer mantle containing the boiling solvent, and so forth, have as their object the securing of a constant heating effect, but in spite of these ingenious contrivances the experimenter is left, to a certain extent, at the mercy of changes in the gas-pressure. This difficulty may be avoided, and the whole apparatus be much simplified by using electricity as the source of heat ; for example, by passing a current through a fine platinum wire immersed directly in the solution of which the boiling-point is desired. An amperemeter in the circuit gives perfectly reliable data as to the absolute number of heat units furnished to the solution in unit time, and if its readings do not vary, the heating effect must be constant.

Such an arrangement obviates the danger of superheating, for the wire gets so hot that little bubbles of vapor are formed while the body of the liquid is yet far below its boiling-point, and the constant presence of some vapor is well known, both theoretically and practically, to be the best possible precaution against superheating. The platinum wire sealed into the bottom of Beckmann's vessel to facilitate boiling, the glass beads, the asbestos stove, the outer mantle for the boiling solvent, and the return-flow condenser attached to the outer mantle, all become unnecessary. When using low-boiling combustible solvents, such as ether and chloroform, there is relative security from breakage and conflagrations. The cost of the electrical energy is far less than one would at first imagine. As will be seen from the experimental part below,

a current of two amperes passing through a resistance of five ohms gives ample heating effect for all ordinary solvents. On the basis of 13.39 cents per thousand watt hours the experiment costs less than one-third of a cent an hour.

The apparatus is shown in the figure. The outer vessel is the same as that used by Beckmann. Later, a large test-tube was substituted for this and, as there was no side arm, the return-flow condenser passed through the cork. The electric connection is furnished by *C, C*, two glass tubes filled with mercury, passing through the cork and reaching nearly to the bottom of the vessel. Rather heavy bits of platinum wire are fused into the ends and turned up to form hooks, for convenience in attaching the fine platinum wire destined to do the heating.

The actual diameter of the platinum wire for the heating coil, *D*, is not important, but obviously the greater the diameter the more wire must be used to obtain a given resistance. A meter of wire, 0.1 mm. in diameter, had a resistance of 23+ ohms at room temperature. Tested as to its carrying capacity, it became red-hot with 1.2 amperes passing through it, white-hot with 1.6 and fused with 1.9 amperes. But immersed in water or any other liquid, it was so effectually cooled that the heaviest current at my disposal, rather more than 5 amperes, did not begin to raise it to redness. Twenty centimeters of this wire were coiled closely around a copper wire scarcely over 1 mm. in diameter, and the spring thus obtained, between 1.5 and 2 centimeters long, had all the stiffness needed and could be bent about to a considerable extent without causing the individual rings to come in contact with each other. In connecting this spiral the free ends were either wrapped round the hooks several times or were sealed



directly into the mercury tubes, thus doing away with the heavier platinum wires. Both plans gave satisfactory contacts.¹

Some care must be taken in so adjusting the spiral at the bottom as not to leave any great length of wire in a perpendicular position. It happened once or twice that vapor forming below rose in such a way as to protect a part of the wire above from actual contact with the liquid, and the part thus protected grew red-hot. Furthermore, caution must be used in putting the apparatus together not to let the bulb of the thermometer touch the sides of the vessel or either mercury tube. If it does, fluctuations in the readings will be observed.

A battery jar, filled with felt, but with a hole left in the middle just big enough for the boiling vessel, was pushed up over the whole apparatus after everything else was in place. This is a simpler and more effective insulation from drafts and from losses of heat by radiation than Beckmann's outer mantle containing boiling solvent. It has this disadvantage, that the boiling cannot be watched. On the other hand, it is not necessary to watch it where the constancy of the heating is so readily observed from the amperemeter, and the behavior of the thermometer gives all the information needed as to when an added portion of substance has dissolved, rising steadily to a point where it remains constant. If it is imperative to look inside, the jar of felt is easily let down, and a short time suffices to establish the former temperature when it is replaced. A Dewar vacuum-jacketed vessel would make an ideal apparatus for this method, offering as perfect insulation as could be desired, and at the same time transparency. Unfortunately, one could not be obtained at the time of carrying out these experiments.

Any constant source of electricity may be used, but for my purpose it was convenient to insert the apparatus in the

¹ The diameter of a spiral of such wire must be small. The first coils were wound over a stirring rod, but they were far too flexible, and neighboring rings could not be prevented from touching each other, thus cutting out a large part of the resistance. The wire was also wound around a glass rod and sealed on permanently. Loops were made at the ends and hung on the hooks, but when boiling began the whole coil was tossed about, making and breaking contact, so that with a high potential current sparking occurred, and the wire sometimes fused.

dynamo circuit in series with the incandescent lamps. With 20 centimeters of 0.1 mm. diameter platinum wire and a current of about 1.8 amperes, the heat was sufficient to boil 30 cc. of water in five minutes. A coil of 10 centimeters of the wire and a current from 3 cells of a storage battery gave excellent results with low-boiling solvents.

It is, perhaps, not the least of the advantages derived from the use of electricity, that the apparatus is so much simpler and less expensive than that now in use. Indeed, it may be put together in a short time from materials at hand in any laboratory.

The process of carrying out an experiment is in every respect identical with Beckmann's method, and need not be entered into. The first experiments had as their object to determine the constancy of the boiling-points obtained with pure solvents.

Experiment I, with Distilled Water.

Time in minutes.	Reading of thermometer.	Barometer.	Amperes.	True boiling-point of water under the observed pressure. ¹
4	water boiling	738.5	1.88	
9	0.842	738.5	1.87	99°.201
19	0.850		1.86	
40	0.854		...	
44	0.856	738.7	1.87	99°.209
49	0.857		...	
88	0.860		...	
90	0.864	739.0	1.87	99°.220
92	0.863		...	
95	0.863		...	
97	0.862	739.0	...	

The readings are not constant, but neither is the atmospheric pressure. The last column shows that the boiling-point of water rises 0°.019 when the pressure rises from 738.5 to 739.0 mm. If we assume that the water reached its true boiling-point some time between nine and nineteen minutes, say at a thermometer-reading close to 0.845, the increased pressure will account for the rise in the boiling-point to 0.864. As the amperemeter varied very little it was often left out in later experiments. It was not absolutely stationary, the

¹ Landolt and Börnstein: Phys. Chem. Tabellen, p. 60.

needle oscillating slightly between limits of + or —0.01 amperes.

Experiment II, with another Sample of Distilled Water.

Time in minutes.	Reading of thermometer.	Barometer.
10	0.790	736.6
20	0.790	736.6
22	0.792	
25	0.790	
30	0.789	
40	0.792	736.6
87	0.792	736.5

The atmospheric pressure did not vary and the constancy of the thermometer readings is all that could be desired.

The rule was adopted in future experiments that to obtain the starting-point, or boiling-point of the pure solvent, the thermometer readings must not vary more than 0°.002 for fifteen minutes before the first portion of the substance is added. Ethyl alcohol, chloroform, and benzene were used as solvents, and there was never any difficulty in fulfilling these conditions when the atmospheric pressure did not change. Usually half an hour, sometimes three-quarters of an hour, elapsed before the first addition of substance.

Beckmann has measured the lowering effect on the boiling-point when glass beads are put in his apparatus.¹ In one of his experiments the addition of 13 grams of the beads lowered the boiling-point from 0°.60 to 0°.24, and they are an essential feature of his method to diminish superheating and bumping, as well as to favor a thorough uniformity of temperature in the boiling liquid. It does not seem possible for superheating to take place to any extent with my modification for reasons already stated, but the beads might help in securing uniformity of temperature. The experiment was tried with benzene as the solvent. The boiling-point was determined, first without, and then after successive additions of beads.

Experiment III, Effect of Beads.

Grams of beads.	Reading of thermometer.
0	1.805
3	1.795
13	1.779
23	1.765

¹ Ztschr. phys. Chem., 21, 239.

An effect is here noticeable, but as it amounts to only $0^{\circ}.040$, in no way comparable to the difference of $0^{\circ}.36$ observed by Beckmann, it is safe to conclude that, while glass beads might be a slight advantage, they are by no means necessary. This is fortunate, for the coil, buried beneath the beads which hindered the free circulation of the liquid, often grew red-hot and several times fused.

A number of molecular weight determinations have been made, and the following examples will suffice to show the nature of the results :

Table I.

Solvent, ethyl alcohol. $K = 11^{\circ}.5$.

Substance, naphthalene. Mol. wt., 128.

Grams solvent.	Grams substance.	Observed raising.	Grams substance in 100 grams solvent.	Molecular weight.	Beckmann. ¹	
					Grams substance in 100 grams solvent.	Molecular weight.
27.0895	0.1601	0.084	0.592	80.9		
	0.4945	0.203	1.82	103.4	2.42	148
	0.8670	0.322	3.20	114.3	4.14	155
	1.1903	0.431	4.39	117.2		
	1.6637	0.572	6.141	123.5		
	2.0920	0.692	7.722	128.3		
	2.5622	0.822	9.458	132.3		
	3.1927	0.984	11.78	137.8		

Table II.

Solvent, ethyl alcohol. $K = 11^{\circ}.5$.

Substance, benzoic acid. Mol. wt., 122.

Grams solvent.	Grams substance.	Observed raising.	Grams substance in 100 grams solvent.	Molecular weight.	Beckmann. ¹	
					Grams substance in 100 grams solvent.	Molecular weight.
28.3919	0.3375	0.188	1.18	72.7	1.98	115
	0.5981	0.286	2.11	84.7		
	0.8885	0.396	3.13	90.9	3.04	121
	1.2469	0.535	4.39	94.4	4.42	124
	1.7926	0.746	6.31	97.3		
	2.4254	0.966	8.54	101.7		
	3.3989	1.297	11.97	106.1		

¹ Ztschr. phys. Chem., 6, 437.

Table III.

Solvent, ethyl alcohol. $K = 11^{\circ}.5$.

Substance, salicylic acid. Mol. wt., 138.

Grams solvent.	Grams substance.	Observed raising.	Grams substance in 100 grams solvent.	Molecular weight.	Beckmann. ¹	
					Grams substance in 100 grams solvent.	Molecular weight.
30.0900	0.1695	0.091	0.563	71.2	1.37	129
	0.4240	0.182	1.41	89.0		
	0.7890	0.300	2.62	100.5	2.76	139
	1.2170	0.431	4.04	107.9		
	1.8589	0.627	6.18	113.3	5.29	140
	2.5876	0.850	8.60	116.3		
	3.5757	1.157	11.88	118.1	13.40	142
	5.0180	1.611	16.68	119.0		
	6.5996	2.121	21.93	118.9	17.29	143

Table IV.

Solvent, chloroform. $K = 36^{\circ}.6$.

Substance, benzoic acid. Mol. wt., 122.

Grams solvent.	Grams substance.	Observed raising.	Grams substance in 100 grams solvent.	Molecular weight.	Beckmann. ¹	
					Grams substance in 100 grams solvent.	Molecular weight.
52.3229	0.1659	0.139	0.317	83.5	0.85	199
	0.6051	0.360	1.16	117.6		
	1.3742	0.673	2.63	142.8	1.73	208
	2.1692	0.980	4.15	154.8		
	3.2744	1.379	6.258	166.1	5.15	220
	4.3140	1.733	8.245	174.1		
	5.7073	2.210	10.91	180.6	8.61	226

These results are uniformly lower than those obtained by Beckmann with the same solvents and substances, as may be seen by comparing his figures, contained in the last two columns, with mine. This is possibly due to the fact that no great pains were taken to purify the solvents, the object not being to duplicate Beckmann's results, but to demonstrate the usefulness of this modification of the boiling-point method. And the regularity of the results demonstrates this sufficiently.

Electric heating is not adapted for use with water solutions, for difficulties due to electrolysis would surely be encountered. This is no serious limitation, for owing to its very small

molecular raising of the boiling-point and its strong dissociating effect, water would never be selected if another solvent could be used. It was feared that complications might arise with other solvents owing to the action of the current. In fact the remarkably low results, obtained with very dilute solutions, seem to point to a form of dissociation, under the conditions of the experiment, of non-electrolytes in solvents to which it is not usual to ascribe a dissociating power. It is my purpose to continue the investigation with a large number of solvents and substances and varying currents to learn more concerning this interesting phenomenon.

The best test of a new method is in its application. Fourteen students were carrying out determinations by the boiling-point method for the first time. Eight used the old form of apparatus and six electric heating. The results obtained by the six were without exception better than those obtained by the eight.

LABORATORY OF PHYSICAL CHEMISTRY,
ANN ARBOR, MICHIGAN, JUNE, 1899.

A CONTRIBUTION TO OUR KNOWLEDGE OF DICARBONYL CUPROUS CHLORIDE.

BY WILLIAM APP JONES.¹

INTRODUCTION.

In attempting to determine the free oxygen in illuminating gas by means of an ammoniacal solution of cuprous chloride, Leblanc, Stas, and Doyère² observed that a large quantity of carbon monoxide and ethylene were also absorbed.

Leblanc then showed that carbon monoxide is absorbed by a hydrochloric acid solution of cuprous chloride, easily and with only a very slight rise in temperature, and the same was found true for an ammoniacal solution. He believed that in both cases the proportion of carbon monoxide to cuprous chloride was 1 : 1.

Leblanc also noticed that by an elevation of temperature or

¹ The work, an account of which is here given, was undertaken at the suggestion of Professor Remsen and carried out under his guidance. The article formed the dissertation submitted by the author to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1898.

² *Compt. rend.* (1850), 30, 483.

by a removal of the atmospheric pressure from these solutions the carbon monoxide was given off as such, and that ammoniacal solutions of the cuprous salts in general have the power to absorb this gas. He did not succeed in isolating any definite compounds from these solutions.

In 1856 Berthelot¹ succeeded in isolating the compound formed by passing carbon monoxide through a cold saturated solution of cuprous chloride in concentrated hydrochloric acid. He obtained beautiful pearly plates which altered very rapidly in the air, making it impossible to prepare them for analysis without at least some loss of carbon monoxide. The figures obtained by his analyses approximated those required by the formula $4\text{Cu}, \text{Cl}_3, 3\text{CO} \cdot 7\text{H}_2\text{O}$, but since the compound alters so rapidly he believed it to be $\text{Cu}_3\text{Cl}_3 \cdot \text{CO} \cdot 2\text{H}_2\text{O}$. Evidently this formula is based upon very unsatisfactory evidence, and the present work was undertaken to determine more accurately, if possible, the composition of the substance, to study its conduct under different conditions of temperature and pressure, and to determine the chemical activity of the carbon monoxide at the moment of its liberation.

PREPARATION OF MATERIAL.

Cuprous Chloride.

This was prepared by the action of *aqua regia* on copper turnings—the latter being in excess. In its preparation about half a liter of concentrated hydrochloric acid was poured into a flask containing 300–350 grams of the copper turnings, and the acid heated almost to boiling. Small quantities of concentrated nitric acid were then introduced from time to time and the heating continued for half an hour, when the hot solution was quickly filtered through asbestos and the cuprous chloride precipitated in the form of a fine white powder by the addition of several liters of cold water. The precipitate was then filtered off quickly and washed from acid, the final washings being made with glacial acetic acid. The material was at once dried in an air-bath, at a temperature of $115^\circ\text{--}125^\circ\text{C}$., for twelve hours. Proceeding in this way it is possible to obtain cuprous chloride perfectly dry and white,

¹ Ann. chim. phys. [3], 46, 488.

and a specimen kept for six months in a glass-stoppered bottle suffered no change in color. The analysis of the material gave the following results:

I. 0.2012 gram material gave 0.1607 gram CuO.

II. 0.2112 gram material gave 0.1692 gram CuO.

	Calculated for Cu ₂ Cl ₂	I.	Pound.	II.
Cu	64.06	63.72		63.94

Preparation of Carbon Monoxide.

The carbon monoxide used in most of the experiments was prepared by the action of sulphuric acid on potassium ferrocyanide, though comparative experiments were made with carbon monoxide obtained by the action of sulphuric acid on formic acid. In both cases the gas was passed through four or five wash-bottles, containing a concentrated solution of caustic potash and, when all the air had been displaced, it was collected in a glass gasometer.

Preparation of Dicarbonyl Cuprous Chloride.

In preparing this compound the cuprous chloride was placed in a small balloon flask, which in turn was immersed in ice-water. The flask was tightly fitted with a three-hole rubber stopper; through one opening a small dropping funnel was passed, and through the others glass tubes, provided with stop-cocks and bent at right angles, one of which was connected with a gas burette, the other with a suction-pump. The dropping-funnel and the tube leading to the gas burette were closed, connection made with the pump, and the flask exhausted. The connection with the pump was closed and enough hydrochloric acid introduced through the dropping-funnel to form a thin paste with the cuprous chloride. The tube leading to the gas burette, which contained carbon monoxide, was then opened and the absorption flask alternately shaken and immersed in ice-water. The absorption, which is at first quite rapid, toward the end becomes very slow, and only after several hours is it complete; frequent shaking is absolutely necessary.

The absorption being complete, ice-water was added, and the crystals which separated were quickly filtered and washed

with ice-water, and then pressed between sheets of drying-paper with a previously cooled spatula. Unless the washing and drying has been done *very* quickly the white plates will have become a green paste, and in any case there will be a slight alteration.

Analysis of the Compound.

Decomposition Method.—As shown above, it is impossible to dry and then weigh the compound for analysis. In the first instance the material was washed and dried as quickly and thoroughly as possible, and then decomposed by an elevation of temperature, the products being either measured or weighed.

The apparatus for the decomposition consisted of a small bulb of about 6 cc. capacity, into which the compound was introduced. This bulb was provided with a two-hole rubber stopper: through one opening was passed a small glass tube, bent at right angles, which extended to the bottom of the flask, and was connected with a calcium chloride tube. This was closed during the decomposition.

A similar glass tube was introduced through the other opening, which extended just below the stopper, and was connected with a weighed calcium chloride tube in which the water given off by the decomposition of the compound was collected. This tube was protected by another calcium chloride tube, the latter being connected with a gas-measuring tube in which the carbon monoxide was to be collected. During the decompositions the little bulb containing the material was immersed to a given-point in a water-bath maintained at 80° C., and blank determinations were previously made to ascertain the correction to be applied to the volume of carbon monoxide collected, the correction being the expansion of the gas in the bulb.

The compound was prepared as previously described, dried very quickly between sheets of drying-paper, and at once transferred to the decomposition bulb, which had previously been weighed. The stopper was at once inserted and connection made with the weighed calcium chloride tube, the protecting calcium chloride tube, and the gas meas-

uring tube. The decomposition bulb was placed in the water-bath, and a temperature of 80° C. maintained until there was no change in the volume of gas collected. This volume was corrected for temperature, pressure, water-vapor, and for the expansion of the gas in the decomposition-bulb. The volume of carbon monoxide having been ascertained, the measuring-tube was disconnected and dry carbon dioxide pressed through the calcium-chloride tube previously closed, and the tube leading to the bottom of the decomposition-flask. This was continued until there was no change in the weight of the weighed calcium-chloride tube, when a final weighing of this tube and the decomposition-bulb was made, giving respectively the weight of the water and cuprous chloride in the compound. From the volume of carbon monoxide collected, its weight was calculated.

While this method is theoretically very simple, it is in reality very difficult on account of the extreme instability of the compound, which makes it almost, if not quite, impossible to dry it without some decomposition. While the method is rather unsatisfactory in the results obtained, yet it was the only one by which it was possible to determine the amount of water present.

The results of three analyses are given on page 292.

Absorption Method.—This method was also employed, as the results obtained were found to be more accurate than those obtained by the former method. From 1 to 2 grams of cuprous chloride were carefully weighed and introduced into an absorption bulb, similar to that described on page 289. The bulb was then closed, immersed to the mark in ice-water, and exhausted. The exhaustion being complete, connection with the pump was closed, enough concentrated hydrochloric acid introduced to form a thin paste with the cuprous chloride, the connection with the gas tube opened, and carbon monoxide allowed to enter, and the volume of gas in the measuring tube was quickly noted as soon as atmospheric pressure was reached in the absorption bulb. The bulb was then alternately shaken and immersed in ice-water until absorption was complete. This required about three hours, and toward the end of this time the flask must be shaken almost con-

I.			II.			III.		
Cu ₂ Cl ₂	0.3280 gram	= 60.78 per cent	0.2180 gram	= 62.21 per cent	0.2170 gram	= 62.41 per cent		
H ₂ O	0.1220 "	= 22.61 "	0.0740 "	= 21.11 "	0.0750 "	= 21.57 "		
CO	0.0896 "	= 16.60 "	0.0584 "	= 16.67 "	0.0557 "	= 16.02 "		
Total	0.5396 "	= 99.99 "	0.3504 "	= 99.99 "	0.3477 "	= 100.00 "		
Same results calculated in terms of Cu ₂ Cl ₂ and CO for comparison with those recorded on page 293.								
I.			II.			III.		
Cu ₂ Cl ₂	0.3280 gram	= 78.54 per cent	0.2180 gram	= 78.87 per cent	0.2170 gram	= 79.57 per cent		
CO	0.0896 "	= 21.45 "	0.0584 "	= 21.13 "	0.0557 "	= 20.42 "		
Total	0.4176 "	= 99.99 "	0.2764 "	= 100.00 "	0.2727 "	= 99.99 "		

stantly. In some instances the bulb was kept in ice-water for several days, being shaken at intervals, but no gas was absorbed after the first three hours, when this part of the operation had received the proper treatment.

Determinations were also made to see if the strength of acid used had any influence on the amount of carbon monoxide absorbed. It was found to have no effect, except that the absorption was the more rapid the more concentrated the acid used. This fact is doubtless due to the greater solubility of both compounds in the stronger acid.

These results led me to try pure water, and, while the absorption is very slow, exactly the same amount of carbon monoxide is absorbed as when hydrochloric acid is used.

When the bulb containing dicarbonyl cuprous chloride is heated to 60° or 70° C., exactly the same amount of carbon monoxide is given off as was originally absorbed. On cooling the bulb it is exactly reabsorbed, and this operation can seemingly be repeated indefinitely. Dry cuprous chloride does not absorb dry carbon monoxide.

I give below four analyses in the order in which they were made :

	Weight Cu_2Cl_2 .	Weight CO absorbed.	Per cent CO.	Remarks.
IV.	2.0006	0.5437	21.37	Cu_2Cl_2 in water
V.	1.0045	0.2703	21.20	Cu_2Cl_2 in $1\text{HCl} : 4\text{H}_2\text{O}$
VI.	1.0069	0.2733	21.35	Cu_2Cl_2 in $1\text{HCl} : 2\text{H}_2\text{O}$
VII.	1.0027	0.2749	21.51	Cu_2Cl_2 in conc. HCl .

I am aware that there is one considerable source of error in this method. The compound formed, as well as the cuprous chloride, is insoluble in water, and only slightly soluble in hydrochloric acid, so that no matter how long the absorption is continued nor how vigorously the bulb is shaken, some unchanged cuprous chloride will always be enclosed in the compound formed, causing the percentage of gas absorbed to be slightly low. The percentage of carbon monoxide required by different formulas is as follows :

$\text{Cu}_2\text{Cl}_2 \cdot \text{CO}$	requires	$\text{CO} = 12.41$
$4\text{Cu}_2\text{Cl}_2 \cdot 7\text{CO}$	"	$\text{CO} = 19.91$
$5\text{Cu}_2\text{Cl}_2 \cdot 9\text{CO}$	"	$\text{CO} = 20.37$
$6\text{Cu}_2\text{Cl}_2 \cdot 11\text{CO}$	"	$\text{CO} = 20.66$
$12\text{Cu}_2\text{Cl}_2 \cdot 23\text{CO}$	"	$\text{CO} = 21.40$
$\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$	"	$\text{CO} = 22.13$

It is evident that the formulas considered probable by Leblanc ($\text{Cu}_2\text{Cl}_2 \cdot \text{CO}$) and the one assigned to the compound by Berthelot ($\text{Cu}_2\text{Cl}_2 \cdot \text{CO} \cdot 2\text{H}_2\text{O}$) cannot be entertained. The percentage of carbon monoxide in $\text{Cu}_2\text{Cl}_2 \cdot \text{CO}$ is only 12.41; the average of more than fifty determinations made by me, and varying from one another by only a few tenths of a per cent, is about 21.4 per cent.

Exactly 21.4 per cent of carbon monoxide is removed by the formula $12\text{Cu}_2\text{Cl}_2 \cdot 23\text{CO}$. While such complex compounds are not unknown in inorganic chemistry, certainly they are quite rare, and while the percentage of carbon monoxide required by $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$ is 22.13, yet there is a constant error in both methods, causing the results to be slightly low, so that it seems to me fair to accept the formula $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$ as highly probable.

As regards the proportion of water present, we must rely entirely on the decomposition method. While this was found to be not as accurate as could be desired, yet there is a certain rough agreement. In three successive determinations the percentages of carbon monoxide found were 21.45, 21.13, and 20.42. These results show that the compound had slightly decomposed in drying, yet the average percentage of carbon monoxide (21.0) is only slightly below the average obtained by the other method (21.4). Keeping the proportions $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$ constant and varying the proportion of water, we obtain:

$\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 3\text{H}_2\text{O}$	contains	$\text{H}_2\text{O} = 17.55$	per cent.
$\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$	"	$\text{H}_2\text{O} = 22.11$	"
$\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 5\text{H}_2\text{O}$	"	$\text{H}_2\text{O} = 26.19$	"

The average percentage of water was found to be 21.76 (page 292), only 0.35 per cent lower than required by $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$. On the other hand it is 4.21 per cent higher than

required by $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 3\text{H}_2\text{O}$ and 4.43 per cent lower than required by $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 5\text{H}_2\text{O}$. This makes it seem highly probable that the composition of dicarbonyl cuprous chloride is expressed by the formula $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$.

Behavior of Dicarbonyl Cuprous Chloride under Reduced Pressure.

Leblanc pointed out that this compound loses carbon monoxide when the atmospheric pressure is removed, yet no exact statement has been made in regard to this point, so experiments were undertaken with this object in view.

The compound was prepared in a bulb of 5 cc. capacity. This bulb was provided with a dropping-funnel having a three-way stop-cock, so that it could be disconnected or connected with a gas measuring tube containing carbon monoxide, and with a Sprengel pump. A manometer was connected with the tube leading to the pump. Blank experiments were made to ascertain the correction, due to the expansion of the air in the bulb and tubes. For this purpose the bulb, containing the same amount of water as that used in the actual experiments, was immersed to the mark in ice-water, and the pump started. The gas pumped out at different pressures was collected in a measuring tube and corrected for temperature, pressure, and water vapor. These corrections are:

Pressure. mm.	Vol. air collected. cc.	Pressure. mm.	Vol. air collected. cc.
460	29.9	130	60.0
360	39.0	100	63.2
260	48.2	60	66.4
160	57.6	40	68.0

The compound having been prepared in the usual manner, it was only necessary to close the connection with the gas burette and open the stop-cock leading to the pump.

The first series, in which dilute acid was used, is as follows:

Table I.

0.5058 gram Cu_2Cl_2 (in $1\text{HCl} : 12\text{H}_2\text{O}$) absorbed 0.1364 gram (109 cc.) Co (= 21.24 per cent).

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	29.99	29.9	0.09	0.07
360	39.40	39.0	0.40	0.35
260	49.20	48.2	1.00	0.87
160	59.80	57.6	2.20	1.92
135	170.16	59.3	111.86	98.12
40	182.01	68.0	114.01	100.00

At each pressure given above the pump was stopped for twenty-four hours to see that the reading was constant, and at the end of a week, at a pressure of 160 mm., only 2.2 cc. of gas had been given off. When the pressure was lowered to 135 mm. bubbles of gas were given off rapidly, and at the end of nine days more 111.86 cc. of gas had been given off. When a constant reading had been obtained the pressure was lowered to 40 mm. and this maintained for a week, but only 2.15 cc. of gas were given off in this time.

Table II.

0.4910 gram Cu_2Cl_2 (in $1\text{HCl} : 12\text{H}_2\text{O}$) absorbed 0.1319 gram (105.5 cc.) CO (= 21.17 per cent).

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.2	29.9	0.3	0.28
360	39.4	39.0	0.4	0.37
260	49.5	48.2	1.3	1.21
160	59.6	57.6	2.0	1.87
135-125	165.6	59.3	106.3	99.42
40	274.9	68.0	106.9	100.00

These two decompositions are given as extremes, the first being exceptionally poor, the last slightly better than the average. In all cases slightly more gas was collected than originally absorbed. It was impossible to dispense with all rubber connections, and although these were kept well covered with shellac, one could hardly expect to prevent diffusion of air into the apparatus when such a low pressure was maintained for three weeks. It seems, therefore, that the compound made in dilute hydrochloric acid is not decomposed until the pressure is reduced to 135-125 mm., and that it is completely decomposed at this point.

Behavior of the Compound Made with Water.

The compound obtained by the absorption of carbon monoxide by cuprous chloride in water, was next submitted to reduced pressure.

Table I.

Co absorbed = 90.05 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.1	29.9	0.2	0.22
360	39.3	39.0	0.3	0.33
260	49.0	48.2	0.8	0.88
160	58.8	57.6	1.2	1.32
130	102.7	60.0	42.7	46.97
100	109.2	63.2	45.7	50.27
60	156.9	66.4	90.5	99.55
40	158.9	68.0	90.9	100.00

By way of explanation, it should be stated that in lowering the pressure from 760-160 mm. only 1.2 cc. of carbon monoxide were given off, but at 130 mm. the evolution of gas increased, and at the end of five days 42.7 cc., or 2.32 cc. less than half the amount absorbed, had been collected when the reading became constant. In lowering the pressure from 130-60 mm. only about 5 cc. of gas were given off, but at 60 mm. the evolution again increased and continued until the compound was decomposed.

Table II.

CO absorbed = 103.33 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.2	29.9	0.3	0.28
360	39.4	39.0	0.4	0.37
260	49.2	48.2	1.0	0.95
160	59.0	57.6	1.4	1.33
130	109.99	60.0	49.99	47.70
100	114.92	63.2	51.72	49.35
60	170.89	66.4	104.49	99.63
40	172.87	68.0	104.87	100.00

Total vol. gas collected
 " " " absorbed

cc.
 104.87
 103.33

Difference

1.54

One-half vol. gas absorbed	cc. 51.66
Vol. gas given off at 130 mm.	49.99
Difference	1.67

It was noticed in these decompositions that a dark coating was formed in the bulb, having a metallic appearance when deposited slowly and in fine condition. This coating gave the copper test distinctly. The fact will be referred to later.

Behavior of the Compound made with Concentrated Hydrochloric Acid.

The results of one determination will show this behavior in a general way.

CO absorbed = 105.2 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
410	40.7	39.2	1.5	1.38
310	60.2	44.7	15.5	14.32
260	74.4	48.2	26.2	24.21
210	91.8	52.9	38.9	36.95
160	117.2	57.6	59.6	55.08
130	168.2	60.0	108.2	100.00

It will be seen from the above that in this instance decomposition begins at about 410 mm. pressure and gradually increases to 160 mm., when it increases more markedly until decomposition is complete at 130 mm.

This decomposition agrees with those in which dilute acid was used in that decomposition is complete at 130 mm.; it differs from both in that marked decomposition begins below 130 mm. The stronger the acid the greater the ease with which carbon monoxide is absorbed, and also giving off again under reduced pressure. These results are discussed and the decompositions expressed in the form of curves on page 310.

Absorption of Carbon Monoxide by Cuprous Chloride in Pyridine.

It was desired to test the effect of increased temperature on some compound of cuprous chloride and carbon monoxide. The compound made with water or hydrochloric acid is too

sensitive to heat to be studied with accuracy. W. Lang¹ has noted that cuprous chloride in pyridine has the power to absorb carbon monoxide; this compound was prepared and found to have the stability desired.

The method of preparation was similar to that described on page 289. No matter how carefully the bulb was exhausted, the instant the pyridine came in contact with the cuprous chloride, both assumed a deep-green color and the bulb became slightly warm. The material showed an annoying tendency to form small hard lumps, and it was necessary to heat to 60° or 70° C. to get these lumps broken and into solution. Complete solution was doubtful even then, as the liquid was so dark that it was impossible to see through it.

Having obtained a solution as nearly perfect as possible, the absorption of carbon monoxide was effected as in the former experiments. The compound formed appeared as shining white plates on the bottom of the bulb and, on the addition of ice-water, more of the material was precipitated. All attempts to filter and dry this compound failed, as the crystals instantly turn green in the air.

As the compound formed by the absorption of carbon monoxide by cuprous chloride in pyridine is too unstable to admit of drying it, recourse must be had to the absorption method. A large number of determinations were made, and below is given a series showing the extremes. The average tended rather to the higher than the lower percentage.

Weight Cu_2Cl_2 .	Weight CO absorbed.	Per cent CO.
1.0005	0.172637	14.71
0.2020	0.035630	14.98
0.2055	0.036319	15.00
0.4036	0.072710	15.26
0.4028	0.076182	15.90
0.2040	0.039030	16.05

It will be seen at once that the results vary quite widely, probably in consequence of the caking of the cuprous chloride, thereby making absorption incomplete. If the relation of cuprous chloride to carbon monoxide is a simple one, it is probably represented by the formula $2\text{Cu}_2\text{Cl}_2 \cdot 3\text{CO}$, since the

¹ Ber. d. chem. Ges., 21, 1584.

percentage of carbon monoxide, as determined, is undoubtedly low.

The percentages required by the simpler hypothetical compounds are the following :

Cu_2Cl_2	CO	requires	CO = 12.41
$2\text{Cu}_2\text{Cl}_2$	3CO	"	CO = 17.57
$3\text{Cu}_2\text{Cl}_2$	5CO	"	CO = 19.15
Cu_2Cl_2	2CO	"	CO = 22.13

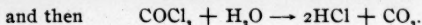
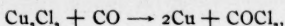
Behavior of the Compound under Increased Temperature.

The method of work was the following : Into a bulb of 25 cc. capacity a weighed quantity of cuprous chloride (about 0.403 gram) was introduced and the bulb closed with a two-hole rubber stopper. Through one opening was passed a dropping funnel and through the other a bent glass tube. The bulb was then exhausted and nitrogen allowed to enter until all air had been displaced, 5 cc. of pyridine introduced, connection made with a gas burette, and the bulb immersed to a given mark in a water-bath, the temperature of which was accurately regulated. As the temperature of the bath was raised, the gas expelled on account of expansion was collected and, at the desired points, the temperature was kept constant for an hour, when final readings were made. The corrections used in the determinations were as follows :

Temperature of bath.	Vol. gas collected. cc.	Temperature of bath.	Vol. gas collected. cc.
0°	0.000	60°	8.592
10°	1.869	70°	10.863
20°	2.849	80°	13.578
30°	3.917	90°	16.739
40°	5.164	100°	21.401
50°	6.767		

In the actual experiments it was always impossible to get off as much gas as was originally absorbed. This may have been influenced by a difference in the vapor-tension of the liquid in the blank and real determinations, or to a reaction between the pyridine and rubber connections, or between the pyridine and cuprous chloride. After each determination the bulb contained a coating of what seemed to be metallic copper, but more abundant than that mentioned previously (page

298). It is conceivable that this reaction had taken place to a slight extent:



If carbon dioxide was formed it was, of course, dissolved by the water in the gas burette, making the readings low.

In the experiments the compound was prepared as previously described, and the decompositions made as in the blank determinations.

Table I.

0.4036 gram Cu_2Cl_2 , absorbed 0.0727 gram (= 58.144 cc. CO) CO (= 15.26 per cent).

Temperature.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
10°	2.717	1.869	0.848	1.45
20°	13.858	2.849	11.009	18.93
30°	22.283	3.917	18.366	31.58
40°	31.188	5.164	26.024	44.75
50°	40.012	6.767	33.245	57.17
60°	47.565	8.592	38.973	67.02
70°	54.571	10.863	43.708	75.17
80°	61.207	13.578	47.629	81.90
90°	68.824	16.739	52.085	89.57
100°	76.029	21.401	54.628	93.95

Table II.

0.4042 gram Cu_2Cl_2 , absorbed 0.0702 gram (= 56.16 cc. CO) CO (= 14.79 per cent).

Temperature.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
10°	4.016	1.869	2.147	3.82
20°	11.849	2.849	9.000	16.02
30°	23.138	3.917	19.221	34.22
40°	28.158	5.164	22.994	40.94
50°	39.015	6.767	32.248	57.42
60°	47.934	8.592	39.342	70.05
70°	53.951	10.863	43.088	76.72
80°	61.831	13.578	48.253	85.92
90°	68.042	16.739	51.303	91.35
100°	74.595	21.401	53.194	94.71

These results are expressed in the form of curves on page 310.

Action of Oxygen on Dicarbonyl Cuprous Chloride.

These experiments were undertaken to determine whether or not the carbon monoxide possess unusual activity at the moment of liberation from the compound. When oxygen, free from carbon dioxide, is passed through dicarbonyl cuprous chloride, even at 0° , the compound instantly turns green, and the gaseous mixture when conducted through baryta water, shows the presence of carbon dioxide. The cuprous chloride contained no material which could give carbon dioxide, for, when oxygen was conducted through this material, suspended in water, and then through baryta water for several hours, not the least precipitate was formed.

Thinking that carbon monoxide might be alternately absorbed and given off, when a mixture of this gas and oxygen is allowed to pass through moist cuprous chloride at 0° , the following method of work was adopted: From 1 to 2 grams of cuprous chloride were placed in a flask and covered with water. This flask was provided with a two-hole rubber stopper, through each opening of which was passed a glass tube bent at right angles, one reaching just below the stopper and the other to the bottom of the flask. The stopper and tubes being in place, the flask was connected with a series of wash-bottles, so that the current of gas used passed first through two wash-bottles containing caustic soda, then through a baryta solution into the cuprous chloride. On issuing from this flask it passed through another bottle containing baryta water, which was protected from the air by a bottle containing a solution of caustic soda. At first pure oxygen was passed through this series for about two hours. The cuprous chloride became slightly green, and neither the baryta solution before or beyond the cuprous chloride flask showed any signs of cloudiness. Without disturbing the apparatus, carbon monoxide was mixed with the oxygen and, when the mixture had been passed for fifteen minutes, a coating began to appear on the entrance tube of the baryta bottle beyond the cuprous chloride flask. At the end of two hours a per-

ceptible precipitate had been formed, while the baryta solution before the cuprous chloride flask remained entirely clear. A determination of the barium carbonate showed that the carbon dioxide formed was less than 1 per cent of the carbon monoxide employed. This experiment was repeated several times, and always with the same result.

The passage of a mixture of oxygen and carbon monoxide over ferrous sulphate or chloride does not cause the formation of carbon dioxide.

Action of Chlorine on Dicarbonyl Cuprous Chloride.

If carbon monoxide possesses unusual activity at the moment of liberation from this compound, we should expect it to show this quite markedly in its conduct toward chlorine. If carbonyl chloride should be formed it would react with the water of crystallization in the compound.

The apparatus consisted of a flask for the preparation of the compound, which was provided with an inlet tube reaching to the bottom, and an outlet tube extending just below the stopper. The outlet tube was connected with a larger tube containing finely powdered antimony, which was in turn connected with a gas measuring tube containing caustic potash. In the preparation of the compound a flask of known size was employed, and the amount of carbon monoxide absorbed was accurately measured. The flask containing the compound was then connected with the antimony tube, and also with a chlorine generator, from which the air had been expelled as completely as possible. When the inlet tube, containing chlorine, was opened, the tube leading from the absorption flask and connected with the antimony tube and gas measuring tube was also opened. The moment the chlorine touched the crystals of dicarbonyl cuprous chloride they turned green and gave off bubbles of gas. The passage of chlorine was continued until all the material had gone into solution, showing complete oxidation of the cuprous chloride. The excess of chlorine was taken up by the antimony and any carbon dioxide formed was absorbed by the caustic soda, while the unchanged carbon monoxide was collected.

At the end of the operation the vessel originally containing

the dicarbonyl cuprous chlorine was filled with water, so as to drive over all the gas contained in it. Knowing the amount of carbon monoxide absorbed, as well as the capacity of the absorption bulb, and hence the volume of free carbon monoxide contained in it after absorption, it was only necessary to subtract the volume of gas collected from the sum of these two to determine the amount of carbon monoxide that had been changed. Blank experiments showed that powdered antimony has not the power of effecting union between carbon monoxide and chlorine. All experiments were performed in diffused daylight.

The rate of flow of the chlorine seemed to affect the amount of carbon dioxide changed, this being greater the slower the current. The same effect was produced by lowering the temperature, thus retarding the decomposition of the compound. For these reasons it was impossible to get entirely concordant results. Below I give an average series of determinations :

CO absorbed. cc.	CO collected. cc.	CO changed. cc.	Per cent changed.
63.2	62.4	0.8	1.26
54.1	52.0	2.1	3.88
69.0	68.4	0.6	0.86
78.6	76.6	2.0	2.54
77.2	73.1	4.1	5.31

From these results it seems that there is a slight reaction between the two gases, but if the carbon monoxide possesses unusual activity, we should expect a greater change than the above figures indicate.

Action of Hydrogen on Dicarbonyl Cuprous Chloride.

Since oxygen has the power to decompose this compound even at and below 0° , it seemed advisable to try the action of hydrogen. The compound was prepared in the usual manner, and the bulb containing it, still immersed in ice-water, was introduced into a system of gas wash-bottles, similar to that described on page 302. Hydrogen, prepared by the action of hydrochloric acid on pure zinc, and then washed with caustic potash, lead acetate, and potassium permanganate, was passed through the compound for eight hours. At the end of this time the crystals had in no way changed their

appearance, and the water contained in the wash-bottles, through which the gas passed on leaving the flask containing the compound, had neither taste nor odor, was neutral in reaction, and did not reduce Tollens' solution in the cold. The compound was then allowed to assume the room temperature, and finally decomposed by warming to 60° , but no change in the carbon monoxide could be detected.

Action of Nitrogen.

These experiments were conducted exactly as in the case of hydrogen. At 0° the compound was not affected by nitrogen, and when the bulb was warmed so as to drive off the carbon monoxide no change whatever could be detected in the latter.

DISCUSSION OF RESULTS.

Action of Oxygen on Dicarbonyl Cuprous Chloride.

There can be no doubt that when oxygen is passed into this compound at 0° it undergoes decomposition, and there is formed simultaneously a small amount of carbon dioxide. This carbon dioxide cannot be due to an impurity in the cuprous chloride, for oxygen passed through the same material gives us no carbon dioxide whatever. Neither can it be due to a peculiar activity of the oxygen brought about by the cuprous chloride through its oxidation, thus causing a splitting of the molecular into atomic or active oxygen, for, when a mixture of oxygen and carbon monoxide is passed through ferrous sulphate or chloride these compounds are oxidized, yet no carbon dioxide is formed. The oxidation of carbon monoxide by the action of oxygen on dicarbonyl cuprous chloride must be due to the activity of the carbon monoxide, or else it is brought about through the agency of the cuprous chloride.

While we have some evidence pointing to the fact that both elements and compounds are unusually active at the moment of their liberation, yet it is far from certain that this activity is a property of the element or compound *per se*. Both heat and electrical phenomena are possibly involved, so that at present we have no satisfactory explanation of the real or apparent activity of the nascent state. If the formation of car-

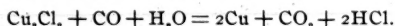
bon' dioxide is due to the activity of the carbon monoxide, it is surprising that this activity is not expressed more strongly toward chlorine.

Drehschmidt has shown¹ that when an ammoniacal solution of cuprous chloride is used for the absorption of carbon monoxide, metallic copper is formed, this being due, as he thinks, to a reduction of the cuprous chloride by the carbon monoxide.

Winkler² shows that caustic potash causes the precipitation of metallic copper from a solution of cuprous chloride containing carbon monoxide; carbon dioxide is formed at the same time.

Winkler also points out³ that by the action of carbon monoxide on a solution of cuprous chloride and palladium chloride, palladium is precipitated and carbon dioxide formed, thus: $\text{PdCl}_2 + \text{CO} + \text{H}_2\text{O} = \text{Pd} + \text{CO}_2 + 2\text{HCl}$. In the absence of cuprous chloride this reaction takes place much more slowly.

As previously stated, in the decomposition of dicarbonyl cuprous chloride by reduced pressure, as well as in the decomposition of the pyridine compound by an elevation of temperature, a coating was formed which had the appearance of metallic copper and gave the test for copper. Considering these facts it seems probable that the formation of carbon dioxide is due to this reaction:



The Constitution and Chemical Nature of Dicarbonyl Cuprous Chloride.

As regards the structure of this compound I have no suggestion to offer. Formulas might be written to satisfy all the bonds of the elements involved, but there is no experimental basis for such a procedure. It seems fairly certain that its composition is represented by the formula $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$. Remembering that both cuprous chloride and carbon monoxide are unsaturated compounds, it does not appear unnatural that they should unite and mutually saturate each other. How the parts are united is a far more difficult question.

¹ Ber. d. chem. Ges., 20, 2754.

² Ztschr. anal. Chem., 28, 272.

³ Loc. cit., 274.

What is more important, and regarding which there is some strong evidence, is a consideration whether the compound is in reality a true chemical individual, an "atomic," as opposed to "molecular," compound. The material has a constant crystal form and luster. It is quite stable at low temperatures in the absence of active substances. If the temperature is elevated or the pressure greatly reduced, it undergoes decomposition, but in a manner similar to compounds, the atomic nature of which is not doubted. In confirmation of this I cite the following cases:

Effect of Pressure Changes on the Molecular Weight of Compounds.

It was observed by Naumann¹ that not only does the density of acetic acid vary with the temperature but also with the pressure, temperature remaining constant.

Acetic Acid—Temperature 100°.

Pressure. mm.	Density.	Pressure. mm.	Density.
393	3.44	168	3.01
342	3.37	156	2.98
258	3.17	130	2.94
232	3.12	92	2.76
186	3.06	77	2.66

Theoretical for $C_2H_4O_2 = 2.073$

" " $C_2H_2O_2 = 4.150$

Similar results were obtained at temperatures ranging from 78°–185°, and the work confirmed by Ramsay and Young² through a much wider range of pressures.

The molecular weight of hydrofluoric acid as determined by Gore³ corresponds to the formula HF. The molecular weight, as determined by Mallet,⁴ at 30° C., is 39.32, almost exactly that required by H_2F_2 . By a more extensive investigation Thorpe and Hambly⁵ have shown that, at the ordinary temperature, the compound is to be expressed by the formula HF. On lowering the temperature the molecule becomes more complex and finally approaches H_2F_2 . The change in

¹ Ann. Chem. (Liebig), 155, 325.

² Jour. Chem. Soc., 49, 790.

³ Ibid., 22, 377.

⁴ This JOURNAL, 3, 189.

⁵ Jour. Chem. Soc., 53, 765, and 55, 163.

density is gradual, there being no sharp breaks, as this series of determinations shows.

Temperature.	Partial pressure. mm.	Vapor-density (H = 1).	Corresponding molec. weight.
32.0°	743	19.87	39.74
32.2°	686	17.89	35.78
31.8°	655	16.99	33.98
32.0°	603	15.41	30.82
32.5°	545	13.89	27.78
32.3°	498	13.27	26.54
31.9°	354	11.50	23.00
32.3°	353	11.39	22.78

Naumann has proved¹ in the case of nitrogen peroxide that for a given temperature the dissociation of N_2O_4 into NO_2 is greater the less the pressure.

Temperature.	Pressure. mm.	Dissociated. Per cent.	Temperature.	Pressure. mm.	Dissociated. Per cent.
18.0°	279	17.3	20.0°	301	17.8
18.5°	136	29.8	20.8°	153	29.3

The Disruptive Influence of Reduced Pressure on Chemical Combinations.

A striking example is afforded by the work of Lemoine on hydriodic acid.² He shows that, with constant temperature, the less the pressure, the smaller the amount of hydrogen and iodine in combination.

Pressure. Atmospheres.	Per cent free H.	Pressure. Atmospheres.	Per cent free H.
4.5	24	0.9	26
2.3	25	0.2	29

Boussingault has proved³ that while oxygen is absorbed by barium oxide at 450°, barium dioxide being formed, if the pressure is then removed, all the oxygen originally taken up is given off again. In other words, by means of a reduction of pressure this transformation is effected, $BaO_2 \rightarrow BaO + O$.

Effect of a Solvent on Dissociation Tension.

Gautier has shown⁴ that dry acid sodium carbonate is only very slightly dissociated in a vacuum of 10–20 mm. at 25°–30°.

¹ Ber. d. chem. Ges., 11, 2045.

² *Ibid.* [5], 19, 464.

³ Ann. chim. phys. [5], 12, 145.

⁴ Bull. Soc. Chim., 26, 115.

If the material is moistened the results are entirely different. When 5 grams of the material were dissolved in 20 grams of water and the solution placed in a vacuum of 300-400 mm. at 25°-30°, at the end of four days the salt was dry and consisted of about 18.7 per cent NaHCO_3 and 81.3 per cent Na_2CO_3 . He found that water exerts the same influence on the dissociation of acid potassium carbonate, and Berthelot and André¹ obtained similar results with acid ammonium carbonate.

It is probable that a similar explanation is to be found for the differences in decomposition of dicarbonyl cuprous chloride. The material is insoluble in water, and in this instance the carbon monoxide is absorbed and given off with the greatest difficulty. It is soluble in hydrochloric acid, and similar to solutions of the acid carbonates of the alkalies, it is then decomposed much more easily. These decompositions can be readily compared by means of the curves on page 310. The break in the curve representing the decomposition of the compound made in water appears somewhat exaggerated. While there undoubtedly is a break, yet it extends only through a very short range of pressure—from about 130-160 mm.—so that a slight error in observation would lead to quite different results. I hardly think this slight irregularity sufficient reason for concluding that, when the compound is prepared in water, 1 molecule of carbon monoxide is united in a manner different from the other.

The decomposition by increased temperature of the compound made in pyridine is exactly similar to the decomposition of acetic acid and nitrogen peroxide, as can be seen from the curves.

Behavior of Inorganic Compounds containing Carbon Monoxide.

The compounds COPtCl_3 , $(\text{CO})_2\text{PtCl}_3$, and $(\text{CO})_3(\text{PtCl})_2$ (Schützenberger²) as well as COPdCl_3 , $(\text{CO})_2\text{PdCl}_3$, and $(\text{CO})_3(\text{PdCl})_2$ (Fink³) can be converted one into another by changing the temperature and proportion of carbon monoxide present and all are decomposed by water, the compounds $(\text{CO})_2\text{PtCl}_3$, $(\text{CO})_3(\text{PtCl})_2$, $(\text{CO})_2\text{PdCl}_3$, and $(\text{CO})_3(\text{PdCl})_2$,

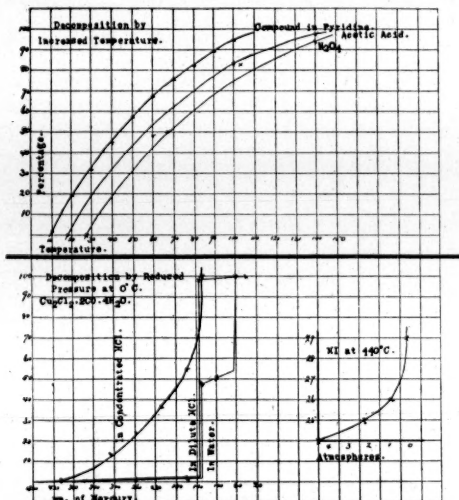
¹ Compt. rend., 103, 665 and 716.

² Ann. chim. phys. [4], 15, 100; and [4], 21, 350.

³ Compt. rend., 126, 646.

giving off part of their carbon monoxide as such—*e. g.*,
 $(\text{CO})_2\text{PtCl}_2 + \text{H}_2\text{O} = \text{Pt} + \text{CO} + 2\text{HCl} + \text{CO}$.

When a solution of COPtCNS.KCNS (Foerster¹) is simply evaporated, the carbon monoxide is set free, and COPtS (Foerster²) is decomposed by reduced pressure. All the compounds of the types COPtCl_2 , $\text{COPt(R)}_2 \cdot 2\text{HCl}$, $(\text{CO})_2\text{Pt(R)}_2 \cdot 2\text{HCl}$ (R = residue of ammonia or primary



base), COPtCNS , COPtS , etc. (Foerster³), are decomposed by the action of potassium cyanide, carbon monoxide appearing as such.

From this very brief review I am sure we can detect great similarity between dicarbonyl cuprous chloride and these compounds, a similarity so great that one could not fail to classify it with them as a true chemical compound.

To the compound $(\text{CO})_2\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ I have given the name

¹ Ber. d. chem. Ges., 24, 2424.

² Loc. cit.

³ Loc. cit.

dicarbonyl cuprous chloride, this being in accord with the name given by Schützenberger to the analogous compound, $(\text{CO})_2\text{PtCl}_2$.

Conclusions.

1. Carbon monoxide is not absorbed by dry cuprous chloride. It is absorbed by cuprous chloride when in hydrochloric acid solution or suspended in water.

2. As a result of this absorption a compound of definite composition is formed. This is represented by the formula $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$.

3. This compound conducts itself like a true atomic compound. It is decomposed by reduction of pressure or elevation of temperature, these decompositions being similar to the decompositions of compounds, the true atomic nature of which cannot be doubted.

4. The carbon monoxide shows no marked increase in chemical activity at the moment of liberation from the compound.

5. From a comparison of dicarbonyl cuprous chloride with other inorganic compounds containing carbon monoxide, it is found to conduct itself in a manner similar to them, and deserves to be ranked as a true chemical compound.

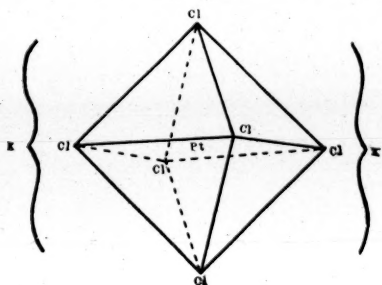
REVIEWS.

WERNER'S THEORY OF THE CONSTITUTION OF INORGANIC COMPOUNDS.

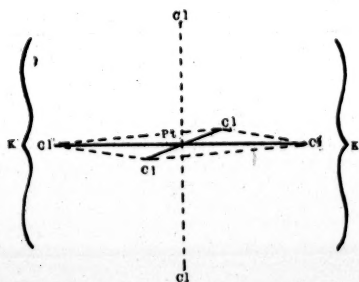
In 1893 Alfred Werner, of Zurich, published his first paper on the constitution of inorganic compounds in the *Zeitschrift für anorganische Chemie*. The theory there advanced, and which has since borne his name, had its origin in the inadequacy of the valence theory to account for the constitution of the metal-ammonia compounds, to which he had been devoting his attention. At this time the theories of Blomstrand as advanced in his "*Chemie der Jetztzeit*" and as modified and developed by Jörgensen, of Copenhagen, were generally accepted as expressing the constitution of these complex bodies. Werner's theory was promptly attacked by Jörgensen, and a vast amount of valuable work has been done by both these chemists in support of their respective views, Jörgensen's eleventh paper and Werner's twentieth paper on the subject having appeared in the *Zeitschrift* the present year. In addition, contributions have been made by several other chemists as K. A. Hofmann, P. Klason, and A. Cossa, while F. Reitzenstein has admirably summed up the whole subject in a recent *Habilitationsschrift*, and has made positive contributions to the subject in his researches on the metal-pyridin compounds. I shall not, in this paper, attempt to review in order the literature of Werner's theory, but rather to show the facts upon which the theory rests, outline the theory itself, and glance at some of the other attempts to solve the problems presented. While, undoubtedly, growing in the first place out of attempts to explain the constitution of the metal-ammonia compounds, and while the battle between Werner and Jörgensen has chiefly taken place on this field,—while, too, a large share of the arguments in support of the theory and in opposition to it have been taken from these compounds, and the theory has been worked out most completely as regards them, the application of the theory is practically to all chemical compounds.

In the metal-ammonia compounds in every well authenticated case the limit of ammonia groups is reached with six to a single positive element; as $\text{Co}(\text{NH}_3)_6\text{X}'$, $\text{Cr}(\text{NH}_3)_6\text{X}'$, etc., where X is the negative element and corresponds in number to the valence of the positive element. In the double cyanides and double nitrites, six is again the limiting number of the cyanogen or nitrite groups, as $\text{Fe}'''(\text{CN})_6\text{M}'$, $\text{Co}(\text{NO})_6\text{M}'$, and here the valence of the positive metal M' corresponds to the valence of the iron or the cobalt in the negative group.

In one of the most common types of crystalline hydrated halides, six is the limiting number of molecules of water of crystallization, as $\text{Ca}(\text{H}_2\text{O})_6\text{Cl}_2$, $\text{Co}(\text{H}_2\text{O})_6\text{Cl}_2$, $\text{Ni}(\text{H}_2\text{O})_6\text{Br}_2$. In these cases Werner considers that these groups, ammonia, cyanogen, nitrite, water are coordinated with the positive element into a group, which acts as a whole, and as a whole possesses a valence depending upon that of the positive element. Since the positive element is here coordinated with six groups, or in other cases, as PtCl_6K_4 , with 6 atoms, it is assumed that these are arranged symmetrically around the positive element, as in the figure of an octahedron, where the positive atom occupies the center and the other elements are at the angles,



or



The elements united with this coordinated group are, as it were, in an outer sphere and are not in direct union with the positive element, which is thus surrounded and in some sense

protected by the groups or elements of the inner sphere. The number and character of the valence of the coordinated group depends in general upon the character of the coordinated groups. Thus we have $\text{Cr}(\text{NH}_3)_4\text{Cl}$, the basic character of the ammonia groups rendering the whole group positive. In $[\text{Cr}(\text{NH}_3)_4\text{Cl}]\text{Cl}$, the group $\text{Cr}(\text{NH}_3)_4\text{Cl}$ is less basic, and has a valence of two. In $[\text{Fe}'''(\text{CN})_4]$ the group containing the negative cyanogen is itself negative and has a valence of three; in $[\text{Fe}''(\text{CN})_4]$ the valence is four. The determination of this valence will be considered later.

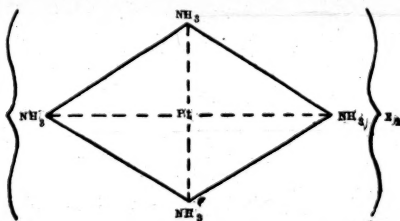
When the molecule is dissolved in water, it is dissociated electrolytically, not into positive and negative elements, but into the coordinated group on the one hand, and that with which it is united on the other hand. In the case of many of the salts this is a familiar fact, for in the old nomenclature we have for ions in solution $[\text{Cr}(\text{NH}_3)_4]_3^+[\text{Cl}]^-$; $[\text{Cr}(\text{NH}_3)_4\text{Cl}]_2^+[\text{Cl}]^-$; $3[\text{K}]^+[\text{Fe}'''(\text{CN})_4]^-$; $4[\text{K}]^+[\text{Fe}(\text{CN})_6]^-$; $2[\text{K}]^+[\text{PtCl}_6]^-$; this being shown both by electrical conductivity determinations and also by the precipitation of these negative ions, whether simple or complex, by silver nitrate. The application of this idea to the case of hydrated salts appears less familiar. In our ordinary halide salts we assume that the halide is directly united to the metal, thus $\text{Na}-\text{Cl}$, and that in solution this is dissociated into sodium ions and chlorine ions. Yet it has been universally agreed that in the ammonia bases the ionized halide atom or other negative group is not directly united to the metal. According to the generally accepted Blomstrand-Jørgensen theory, a halogen directly connected with the metal is not ionizable, but only such as are connected with it through the medium of ammonia. Thus, in the salts of the purpureo series as $[\text{Cr}(\text{NH}_3)_4\text{Cl}]\text{Cl}$, the two chlorine atoms which are connected with chromium indirectly are alone precipitated by silver nitrate in the cold, while the other chlorine atom which is directly connected with the chromium is not thus precipitable, nor is it dissociated in solution. Now the old theory makes no pretense of resolving the inconsistency that, in the one case, a chlorine atom directly united to a metal is not ionizable, while in the other case it is. According to Werner, when, for example,

$\text{Co}(\text{H}_2\text{O})_6\text{Cl}_2$ is dissolved in water, the ions are not $[\text{Co}]$ and $2[\text{Cl}]$, but are $[\text{Co}(\text{H}_2\text{O})_6]^{2+}[\text{Cl}]^-$. Here as in the ammonia bases, the halogen is not directly connected with the metal, but with the group $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, in which the cobalt atom is surrounded by the water molecules in the inner sphere, and,

so to speak, protected by them from direct contact with the halogens.

In order then that a salt may become dissociated in solution, it is necessary that the metal shall be surrounded by a number of other units which may be ammonia or cyanogen, or nitrite groups or single atoms (as the single chlorine atom in the purpureo salts), but which are most frequently water molecules. It is interesting to note that in this point Werner's theory, while availing itself of the theory of electrolytic dissociation in aqueous solution, approaches very closely to the general principles of the hydrate theory of solutions; indeed it really harmonizes the two apparently irreconcilable and mutually exclusive theories, both of which rest upon a substratum of undeniable facts.

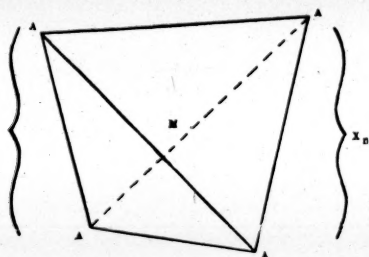
Not all compounds can be explained, however, according to the type $M(A)_6$. In the platinum-ammonia bases, for instance, the limiting number of the ammonia groups appears to be four for each platinum atom, and among the metal-ammonia compounds in general we find very common the type $M(NH_3)_4X_2$. Here there are four groups or atoms directly coordinated with the positive element. This is explained by assuming a configuration of the molecule in a plane; that is, one axis, in the figure of the first type, is wanting. Thus:



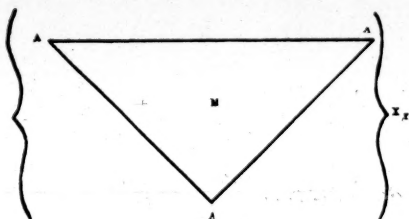
Of this type we have in other classes of compounds $[Pt(CN)_4]K_2$, $[CuCl_4]K_2$, $[Cu(NO_2)_4](NH_4)_2$, $[HgBr_4]K_2$, $[Cd(NH_3)_4]Br_2$, $[Cd(H_2O)_4]Cl_2$, $[Mn(H_2O)_4]SO_4$, and many others. Compounds of this type may pass into those of the first type by two further groups or atoms becoming coordinated with the positive element, as in the formation of the platino-bases from the platino-bases, $[Pt(NH_3)_4]Cl_2$, $[Pt(NH_3)_4]Cl_2Cl_2$; $[Cu(NH_3)_4]Cl_2$, $[Cu(NH_3)_4]Cl_2$, and $[Cu(NH_3)_4](H_2O)_2Cl_2$.

These two types have been most completely worked out by Werner, but there seems to be evidence of the existence of perhaps several other types. Thus, while some compounds

of the second type, $[MA_n]X_n$, may be represented by the plane configuration, in other cases the coordinated group may be represented by the tetrahedron. To this latter, which would be of the same general formula $[MA_n]X_n$, there would correspond a plane configuration of the type $[MA_n]X_n$, or graphically



and



This need not indeed exhaust the possibilities, but thus far no compound seems to have been noticed in which one atom has a higher coordination number than six.

There seem to be several factors which have an influence in determining the coordination number of an element. The nature of the individual atom, that of the coordinated groups or atoms, and that of the atoms or groups of the outer sphere, are all of influence, though insufficient work has as yet been done to determine the relative importance of each factor. That the molecular weight of the coordinated groups is of influence is shown by Reitzenstein's comparison of the hydrates, ammonia compounds and pyridine compounds. While in many cases there is great resemblance between the

two former, and at least one series is known, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot \text{NH}_3 \cdot 4\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 3\text{NH}_3 \cdot 2\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$; and $\text{CuSO}_4 \cdot 5\text{NH}_3$, in which each transition stage from the hydrate to the ammonia compound is known, in the case of pyridine the coordination number in only two cases reaches a maximum of six, these being $[\text{CdPyr}] \text{Br}$, and $[\text{CdPyr}] \text{I}$. Here too the influence of the halogen is apparent, for all efforts have failed to obtain a cadmium chloride containing more than 2 molecules of pyridine. A salt $[\text{CoPyr}_6(\text{H}_2\text{O})_2] \text{Cl}$ is, however, known, and in several of the ammonia-pyridine-platinum bases, the coordination number of the platinum atom is six, though in no case are more than four pyridine atoms present.

Two influences must necessarily affect the coordination number: one, the size of the coordinated group or atom, or perhaps we should better say the space it occupies, a point to which no inconsiderable attention has been given of late years as regards the carbon atom; and the other the character and intensity of its motion. Perhaps also the relative kind and phase of the motion of the central atom and of those coordinated with it may play a part, as suggested by Venable in his recent paper on the nature of valence.

Having thus sketched Werner's theory in broad outlines, we must next examine its application to certain classes of compounds, to gain a more complete knowledge of it and to see how far it is consistent with facts.

Type $[\text{MA}] \text{X}_n$.—Taking up first this type, especially in its application to the metal-ammonia compounds of the type $[\text{MA}] \text{X}'$, we find an almost complete series of compounds, each with successively one ammonia group less than the preceding. The luteo salts $[\text{M}(\text{NH}_3)_6] \text{X}_n$, for example, $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$, by loss of one ammonia group pass into the purpureo salts $[\text{M}(\text{NH}_3)_5] \text{X}_n$. But in the purpureo salts only two of the chlorine atoms are ionized in solution. We should

therefore represent these salts as $[\text{M}_X^{(\text{NH}_3)_5}] \text{X}_n$. The xantho salts as $[\text{Co}^{(\text{NH}_3)_5}_{\text{NO}}] \text{X}_n$ are of this class.

Next come the croceo salts, $\text{M}(\text{NH}_3)_4 \text{X}_n$, and here but one halogen is ionized, hence the formula $[\text{M}^{(\text{NH}_3)_4}_{(\text{NO})}] \text{X}_n$.

In $[\text{Co}^{(\text{NH}_3)_4}_{(\text{NO})}]$ we have, according to Werner, a compound which is not a conductor of electricity and hence is not electrolytically dissociable. In the next group we find $[\text{Co}^{(\text{NH}_3)_3}_{(\text{NO})}] \text{K}$, and $[\text{Co}^{(\text{NH}_3)_3}_{(\text{SCN})}] \text{NH}_4$; and in the last

member of the series many salts of the general type $[MX_n]R'_n$, such as $[Co(NO)_3]K_3$; $[Fe(CN)_6]K_4$; $[CrF_6]K_3$; $[Fe(SCN)_6]K_4$; and $[RhCl_6]K_3$. In this series we notice that as each ammonia group is removed, an atom of the outer sphere replaces it in the coordinated group, and hence the valence of the coordinated group is lessened by one. With the removal of three ammonia groups the basicity of the coordinated group disappears, and its valence becomes zero. With the further removal of ammonia it becomes positive, and the positive valency increases step by step. Thus the valence of the coordinated group is equal to the valence of the central atom minus the number of negative atoms or groups coordinated with it, a negative number representing valence toward positive elements.

A second class of compounds of the type $[M(NH_3)_n]X_n$ is that derived from quadrivalent metals. This class includes the great number of the platini-ammonia bases, as well as ammonia compounds of quadrivalent tin, titanium, and silicon. Examples of the member with the largest number of ammonia groups are $[Pt(NH_3)_6]Cl_4$, $[Sn(NH_3)_6]I_4$, $[Ti(NH_3)_6]Cl_4$, $[Si(NH_3)_6]Cl_4$. From this formula may be derived, by loss of ammonia, compounds similar to those of the first class. Few of these are as yet known. Joly's tetrammonium-nitroso-

ruthenium base, as $\begin{bmatrix} NO \\ Ru \\ OH \\ (NH_3)_4 \end{bmatrix} Cl_2$ and $\begin{bmatrix} NO \\ Ru \\ Cl \\ (NH_3)_4 \end{bmatrix} Cl$,

probably belongs to the division, in which two of the ammonia groups are lost, being replaced by un-ionizable groups or elements. The next division is represented by the platimono-diammine bases $[Pt \begin{smallmatrix} Cl \\ < \\ (NH_3)_4 \end{smallmatrix}] Cl$, where there is but one ionizable chlorine atom. The plati-ammine salts, as $[Pt \begin{smallmatrix} (NH_3)_4 \\ Cl \end{smallmatrix}]$ can be heated with concentrated sulphuric acid without losing chlorine, and hence represent the case where, by the loss of four ammonia groups, all four chlorine atoms have become coordinated with the platinum atom.

In the next division is the salt $[Pt \begin{smallmatrix} NH_3 \\ Cl \end{smallmatrix}] K$, when by the loss of a further ammonia group the whole coordinated group has become negative and univalent. The salt $[Pt \begin{smallmatrix} Pyr \\ Cl \end{smallmatrix}]$ Pyr may also be placed here, though the formula suggested for it by Jörgensen is much more complex. The limiting member of this class is $[MX_n]R_n$, to which belong the familiar salts $[PtCl_4]K_2$, $[SiF_6]K_4$, $[TiF_6]K_3$, $[SnF_6]K_4$, and $[Ru \begin{smallmatrix} NO \\ Cl \end{smallmatrix}] K_2$,

as well as many others. Incidentally I may add that in accordance with the analogy $\text{AuCl}_3 \cdot \text{KCl}$, $\text{PtCl}_2 \cdot 2\text{KCl}$, $\text{RhCl}_3 \cdot 3\text{KCl}$, we should be led to expect $\text{PtCl}_4 \cdot 4\text{KCl}$ and $\text{RuNOCl}_3 \cdot 3\text{KCl}$, or $\text{RuNOCl}_4 \cdot 4\text{KCl}$, yet, as a matter of fact, the number of halogen atoms in the double halides of quadrivalent metals is always limited to six, a fact difficult to account for on the valence theory, and in which it seems necessary to consider the space relations of the atoms.

The third class of compounds, of the type $[\text{M}(\text{NH}_3)_6]\text{X}_n$, is that in which M is a bivalent metal and the number of negative atoms is consequently also two. The number of compounds known in this field is much smaller than in the former cases, though it may well be that when the complex compounds are studied from the standpoint of the Werner theory, many of the theoretically possible compounds will be discovered. Of the first division of this class a very considerable number of compounds are known, as $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$, $[\text{Cu}(\text{NH}_3)_4]\text{Br}_2$, $[\text{Cd}(\text{NH}_3)_6](\text{NO}_3)_2$, $[\text{Co}(\text{NH}_3)_6]\text{SO}_4$, and many others. To the last division of the class, where all the ammonia has been removed and hence replaced by negative groups, the coordinated group therefore becoming negative and quadrivalent, we have the familiar class of double cyanides, as $[\text{Fe}(\text{CN})_6]\text{K}_4$, $\text{Cr}[(\text{CN})_6]\text{K}_4$, $[\text{Ru}(\text{CN})_6]\text{K}_4$, as well as such salts as $[\text{Ni}(\text{NO})_6]\text{K}_4$, and $[\text{CdCl}_6]\text{K}_4$. Of the intermediate divisions, Werner has found but a single representative, $[\text{Cu}(\text{NH}_3)_5]\text{Cl}(\text{NH}_3)_2$.

There is another class of compounds of this first general type in which the ammonia groups have been, to a greater or less extent, replaced by water, the compounds to which Palmar has given the name aquo-ammonia bases. When one of the ammonia groups is substituted by water we have the roseo compounds which are known in the cobalt, chromium, rhodium, and iridium series, of which $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}$ is an example. In these compounds the water is very different from water of crystallization, and cannot be removed without changing completely the character of the salt. In the roseo-tetrammine salts of Jörgensen, we have two ammonia groups replaced by water, without affecting the valence of the coordinated group, as $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$. Salts where 3 molecules of water are replaced by water are known, and the limiting member where all the six ammonia groups are replaced by water belongs to a very common type, as $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$. Of the other classes of this type, numerous compounds are known in which

the ammonia is more or less replaced by water, and the final member, where all the ammonia is thus replaced, brings us to the commonest type of hydrate, as $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}$, $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}$, $[\text{Sr}(\text{H}_2\text{O})_6]\text{Br}$, $[\text{Sr}(\text{H}_2\text{O})_6](\text{IO})_2$, $[\text{Sr}(\text{H}_2\text{O})_6]\text{S}_2\text{O}_8$, $[\text{Zn}(\text{H}_2\text{O})_6]\text{S}_2\text{O}_8$, etc. From this Werner draws the conclusion that the property of metallic salts to unite with 6 molecules of water and with 6 molecules of ammonia, has the same cause, and that this cause rests in the nature of the metallic atom.

Certain familiar salts do, however, unite with more than 6 molecules of water, especially many of the vitriols. Thus we have, for example, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Here, however, the acid radical plays a part, as it is well known that several hydrates of sulphuric acid exist. One of these water molecules can be considered as being united structurally with the SO_4 group, indeed, as a matter of fact, the compound holds one of these water molecules with much more firmness than the other six. This we should write $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$ or $[\text{FeSO}_4(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$. The number of 6 molecules of water recurs again in the double sulphates, where we have

$[\text{Fe}(\text{H}_2\text{O})_6] \begin{matrix} \text{SO}_4\text{K} \\ \text{SO}_4\text{K} \end{matrix}$, etc. The alums form an exception to

this rule, but may be explained by assuming that in some cases the double water molecule acts as a unit, as it is believed to do in water itself. Thus an alum will have the formula

$[\text{M}(\text{H}_2\text{O})_6] \begin{matrix} \text{SO}_4 \\ \text{SO}_4\text{R} \end{matrix}$, the number six again appearing.

Finally, to this first general type belong also a large number of salts in which more or less water is present in the co-ordinated group. Space permits only mere mention of examples. Of the type $[\text{M} \begin{matrix} (\text{H}_2\text{O})_6 \\ \text{X} \end{matrix}] \text{X}$, we have one form of chromium chloride, in which only two-thirds of the chlorine can be precipitated by silver nitrate. Of the type $[\text{M} \begin{matrix} (\text{H}_2\text{O})_6 \\ \text{X}_2 \end{matrix}]$

we have a chromium sulphate, $[\text{Cr} \begin{matrix} (\text{H}_2\text{O})_6 \\ \text{SO}_4 \\ \text{SO}_4 \\ \text{SO}_4 \end{matrix}]$, of which Recoura

has shown that in the freshly prepared solution no precipitate is formed by barium chloride. The type $[\text{M} \begin{matrix} (\text{H}_2\text{O})_6 \\ \text{X}_2 \end{matrix}] \text{R}$ has as example $[\text{Au} \begin{matrix} \text{Cl}_2 \\ (\text{H}_2\text{O})_6 \end{matrix}] \text{K}$, etc. The double salts of the

formula $\left[M \begin{smallmatrix} H_2O \\ X \end{smallmatrix} \right] K$, are very common, as $\left[Cr \begin{smallmatrix} F \\ H_2O \end{smallmatrix} \right] K$, $\left[Al \begin{smallmatrix} Cl \\ H_2O \end{smallmatrix} \right] K$, $\left[Rh \begin{smallmatrix} Cl \\ H_2O \end{smallmatrix} \right] (NH_4)$, $\left[Mn \begin{smallmatrix} F \\ H_2O \end{smallmatrix} \right] [Co(H_2O)]$.

Among the double salts of bivalent metals we find the following: Of the type $\left[M \begin{smallmatrix} (H_2O) \\ X \end{smallmatrix} \right] R$ we have

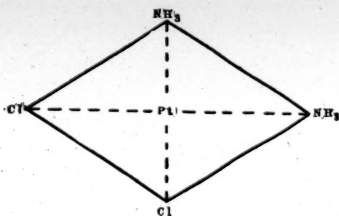
$\left[Mn \begin{smallmatrix} Cl \\ (H_2O) \end{smallmatrix} \right] Li$, $\left[Cu \begin{smallmatrix} Cl \\ (H_2O) \end{smallmatrix} \right] K$, etc.; of the type $\left[M \begin{smallmatrix} (H_2O) \\ X \end{smallmatrix} \right] R$, we have $\left[Fe \begin{smallmatrix} Cl \\ (H_2O) \end{smallmatrix} \right] K$, $\left[Co \begin{smallmatrix} F \\ (H_2O) \end{smallmatrix} \right] (NH_4)$, etc. The sub-

stance of the matter regarding the compounds of this first general type is summed up by Werner in these words. In the metal-ammonia salts, as well as in the hydrates (as far as concerns the normal compounds) and also in the double salts thus far considered, we must assume the group MA_4 , in which all the ammonia molecules, water molecules, or acid radicals are directly connected with the metal atom, since it is in no other way possible to account for their reciprocal relations.

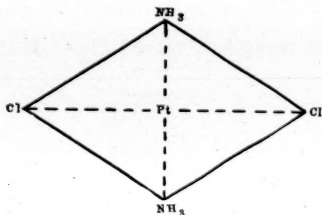
Type $[MA_4]X_n$.—A second type of compounds must now be considered in which the number four appears to play the same rôle as the number six in the first type. These are the compounds in which the metal is coordinated with four groups, and may be derived from the octahedral conformation by the loss of one axis, and hence the group will have a plane configuration, or it may in other cases be considered as represented by the tetrahedron. It is probable that both forms exist in different compounds, and the group may perhaps pass from one form to the other. It is unnecessary to dwell upon this type at length, as its theory will be easily understood from the extended description of the compounds of the first type. The ammonia compounds of this type are numerous, and include the plato-diammine salts $[Pt(NH_3)_4]X_n$, as well as the corresponding diammine salts of palladium. Here also belong many other metal-ammonia salts as $[Cu(NH_3)_4]Cl$, $[Ni(NH_3)_4](SCN)_2$, etc. With the loss of one ammonia we

have the platomonodiammine salts $\left[Pt \begin{smallmatrix} (NH_3) \\ Cl \end{smallmatrix} \right] Cl$, which form with chloroplatinous acid the salt $\left[Pt \begin{smallmatrix} (NH_3) \\ Cl \end{smallmatrix} \right] Pt''Cl_4$, and not $Pt(NH_3)_2.PtCl_4$, which would be the case if both atoms of chlorine were ionizable. To the division $\left[M \begin{smallmatrix} (NH_3) \\ X \end{smallmatrix} \right]$ belong the platosammine and the platosemidiammine compounds $\left[Pt \begin{smallmatrix} (NH_3) \\ Cl \end{smallmatrix} \right]$. Neither of these compounds unites with chloroplatinous acid, and hence both must be ranked as neutral

compounds, as would be expected from Werner's theory. Their isomerism is explained by Werner as stereoisomerism, the platosammine chloride being the *cis* form



and the platosemidiammine chloride being the *trans* form



Two salts recently discovered by Cossa complete the series. These are $\left[\text{Pt} \begin{smallmatrix} \text{NH}_3 \\ \text{Cl}_2 \end{smallmatrix} \right] \text{K}$ and $\left[\text{Pt} \begin{smallmatrix} \text{PyT} \\ \text{Cl}_2 \end{smallmatrix} \right] \text{K}$. Here the loss of the third ammonia group and entrance into the coordinated group of the third negative atom, render the group itself negative and univalent. Finally we have the last division, where all the ammonia is replaced by negative atoms or groups, in the familiar type $[\text{MX}_3]\text{R}_3$, of which $[\text{PtCl}_3]\text{K}$, $[\text{Cu}(\text{NO}_2)_3](\text{NH}_4)_3$, $[\text{Pd}(\text{CN})_3]\text{K}$, $[\text{Hg} \begin{smallmatrix} \text{I}_2 \\ \text{Br}_2 \end{smallmatrix}]\text{K}$, $[\text{Pt}(\text{NO}_2)_3]\text{K}$, are a few of the many examples which might be cited.

In this type also the ammonia can be replaced, as in the first, by water. This is perhaps as well illustrated by the copper sulphate series as any, when we have $[\text{Cu}(\text{NH}_3)_3]\text{SO}_4 \cdot \text{H}_2\text{O}$,

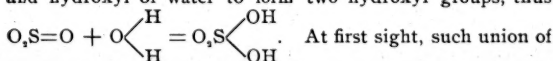
$\left[\text{Cu} \begin{smallmatrix} (\text{NH}_3)_2 \\ \text{H}_2\text{O} \end{smallmatrix} \right] \text{SO}_4 \cdot \text{H}_2\text{O}$, $\left[\text{Cu} \begin{smallmatrix} (\text{NH}_3) \\ (\text{H}_2\text{O})_2 \end{smallmatrix} \right] \text{SO}_4 \cdot \text{H}_2\text{O}$, $\left[\text{Cu} \begin{smallmatrix} (\text{NH}_3) \\ (\text{H}_2\text{O}) \end{smallmatrix} \right] \text{SO}_4 \cdot \text{H}_2\text{O}$, and $[\text{Cu}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$, though many other examples are known. Finally, we have as hy-

drated salts of this type $[\text{Co} \begin{smallmatrix} \text{F} \\ \text{H}_2\text{O} \end{smallmatrix}] \text{K}$, $[\text{Sn} \begin{smallmatrix} \text{Br} \\ \text{H}_2\text{O} \end{smallmatrix}] \text{K}$, $[\text{Hg} \begin{smallmatrix} \text{Cl} \\ \text{H}_2\text{O} \end{smallmatrix}] \text{K}$, etc., members of the other divisions not being known.

That other types than the two thus far discussed may exist is by no means improbable, indeed there is reason to believe that certain elements as columbium and uranium may in certain cases have a coordination number of eight, but such cases have not been worked out thus far.

It seems quite possible that certain elements as nitrogen and boron have the coordination configuration of the tetrahedron with the coordination number of four. Here boron being more positive than carbon, when coordinated with negative atoms, furnishes a negative group as $[\text{BF}] \text{K}$; while nitrogen being more negative than carbon, forms a positive coordination group, as $[\text{NH}_4] \text{Cl}$ and $[\text{N}(\text{C}_2\text{H}_5)] \text{Cl}$. In both cases the valence of the group is the difference between the valence of the element and that of the elements or groups with which it is coordinated.

Thus far the application of the theory of Werner to one large class of compounds, the oxygen salts, has not been touched upon, and this must now be considered briefly. According to the ordinary theories there are two classes of oxides, the acid-forming and the base-forming oxides. A salt is formed by the union of one oxide of each class, but as the terms acid-forming and base-forming are only relative, a salt may be defined as the compound formed by the union of two oxides. Similarly an acid, which is a hydrogen salt, is formed by the union of an acid-forming oxide with water. According to the valence theory, in the formation of an oxy-acid there is assumed the tendency of the doubly-bound oxygen atom of the oxide to unite with the separated hydrogen and hydroxyl of water to form two hydroxyl groups, thus



two oxides to form a salt would seem to have little in common with the union of two chlorides to form a double chloride, but in reality the two reactions are analogous. That salt and acid formation is not dependent upon hydroxyl formation, is rendered probable by two facts. First, considering the union with water to form acids, not all oxides of so-called negative nature will unite with water. The oxides RuO_4 and OsO_4 , for example, in spite of their extreme amount of oxygen, are not acid-forming but neutral substances, and will not unite with water. Second, the union of oxides with water is always (save perhaps exceptionally in the per-iodic acids) limited to the formation of compounds with four atoms of oxygen.

Thus, according to the valence theory, there is no reason why SO_2 should not form H_2SO_4 and P_2O_5 should not form $\text{H}_4\text{P}_2\text{O}_7$. Further, we find that the halogen compounds unite with water as well as the oxides, though the valence theory is responsible, for our habit of considering as of entirely different character these compounds which are really analogous.

Thus far, in considering the coordinated atoms and groups, these have been confined to either non-valent or saturated groups such as water and ammonia, and to univalent elements or groups such as chlorine. The first question which arises is whether a bivalent atom like oxygen entering a co-ordinated group will replace one or two of the groups or atoms we have been considering. This question would seem to be settled by the considerable class of oxyfluorides, where we

have such a substitution; thus $[\text{VF}_6]\text{K}_2$, $[\text{VOF}_5]\text{K}_2$, $[\text{VOF}_4(\text{H}_2\text{O})]\text{K}_2$, $[\text{MoF}_5(\text{NH}_3)]$, $[\text{MoF}_4(\text{H}_2\text{O})]\text{K}_2$, $[\text{MoF}_3(\text{NH}_3)]$, as well as similar compounds of tungsten and

columbium. We have also the compounds $[\text{Mo}(\text{CN})_2\text{O}_2]\text{K}_2$ and $[\text{Mo}(\text{CN})_2\text{S}_2]\text{K}_2$, all of which show that, when oxygen or sulphur enters the coordinated group, it occupies one place only, that is one coordination position. We come thus to the conclusion that the formation of oxy-salts is to be attributed to the same cause as the formation of the so-called coordination compounds which we have already considered. Thus, com-

paring them, we have $\text{OS} + \text{OH}_2 = \begin{bmatrix} \text{O} \\ \text{OSO} \\ \text{O} \end{bmatrix} \text{H}_2$, similar to

$\text{ClAu} + \text{ClH} = \begin{bmatrix} \text{Cl} \\ \text{ClAuCl} \\ \text{Cl} \end{bmatrix} \text{H}$. Indeed, we can cite the forma-

tion of compounds of intermediate type, thus justifying our placing the two above reactions in the same class. For ex-

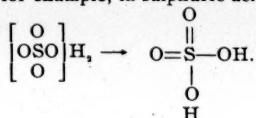
ample, $\text{OCr} + \text{ClK} = \begin{bmatrix} \text{O} \\ \text{OCrCl} \\ \text{O} \end{bmatrix} \text{K}$ and $\text{FAl} + \text{O}(\text{C}_2\text{H}_5)_2 =$

$\begin{bmatrix} \text{F} \\ \text{FAlO} \\ \text{F} \end{bmatrix} (\text{C}_2\text{H}_5)_2$.

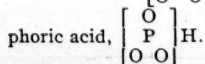
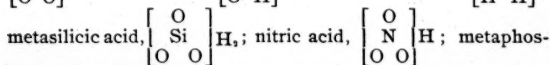
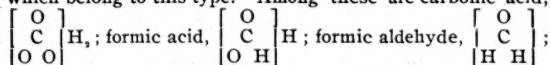
What has here been said will apply equally well to all oxy-salts. In by far the largest number of cases the type of the coordination group is MO_2 . Thus we have $[\text{SiO}_2]\text{H}_2$,

$[\text{PO}]_2\text{H}_2$, $[\text{SO}]_2\text{H}_2$, $[\text{ClO}]_2\text{H}_2$, and $[\text{RuO}]_2$, and in passing thus from the fourth to the eighth group of the periodic table, it becomes apparent why RuO_2 forms no salts. It is also seen that the oxygen number remains the same while the number of hydrogen atoms decreases, although according to the valence theory the valence of the elements regularly increases until the valence of ruthenium reaches eight. The coordination type of $[\text{MO}_2]$ appears to occur in only a single instance, that of the per-iodates, $[\text{IO}_2]_2\text{H}_2$, and $[\text{IO}_2]_2\text{Ba}_2$.

The oxy-salts are thus to be considered as molecular compounds, even as the double halides, and in this same category we have the sulphur, selenium, and probably the tellurium salts. It is perhaps the greatest advantage of Werner's theory that it furnishes a general principle to include all of these compounds, which, though chemically analogous, are by the valence theory explained in very different ways. It is not at all impossible that in some cases these molecular compounds, conditioned by the bivalence of oxygen and the rapid motion of the hydrogen atom, can go over into true valence compounds, as, for example, in sulphuric acid,



If we now consider the spacial configuration of the coordinated group $[\text{MO}_2]$, the tetrahedron seems probable, and we might expect to find the corresponding plane configuration. There are indeed quite a considerable number of compounds which belong to this type. Among these are carbonic acid,



The case of the derivatives of the polymerized oxides would be explained by two or more oxides becoming coordinated, thus $\text{O} \begin{array}{c} \text{O} \end{array} \text{Cr} + \text{O} \begin{array}{c} \text{O} \end{array} \text{Cr} = \text{O} \begin{array}{c} \text{O} \end{array} \text{Cr} \cdot \text{O} \begin{array}{c} \text{O} \end{array} \text{Cr}$ and in the cases where the polymerized oxides are stable, we should have the formation of

the salt as follows:
$$\begin{array}{c} \text{O} \quad \text{O} \\ \text{OCr} \cdot \text{OCr} + \text{OK}_2 = \left[\begin{array}{cc} \text{O} & \text{O} \\ \text{OCr} \cdot & \text{OCrO} \\ \text{O} & \text{O} \end{array} \right] \text{K}_2. \end{array}$$

This conception of the salt corresponds to the ready method

of forming it,
$$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\ \text{K}_2\text{O} \cdot \text{CrO} + \text{CrO} = \text{K}_2\text{O} \cdot \text{CrO} \cdot \text{CrO} \text{ and } \text{K}_2\text{O} \cdot \text{SO} + \end{array}$$

$$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\ \text{SO} = \text{K}_2\text{O} \cdot \text{SO} \cdot \text{SO}. \end{array}$$

The case is the same in the halogen salts where we have similarly
$$\begin{array}{c} \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\ \text{ClAu} + \text{ClK} = \text{ClAu} \cdot \text{ClK} ; \text{Cl} \cdot \text{Au} + \text{ClAu} = \end{array}$$

$$\begin{array}{c} \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\ \text{ClAu} \cdot \text{ClAu} ; \text{ and } \text{ClAu} \cdot \text{ClAu} + \text{ClK} = \text{ClAu} \cdot \text{ClAu} \cdot \text{ClK}. \end{array}$$

That these polymerized halides are sometimes very stable is shown by the vapor-density of aluminum chloride.

It is to be noted further that while with some elements the limiting coordination number is six and with others four, this end type of spacial or plane configuration is not always reached. Owing to less energy of the uniting molecules or other causes, the limit may be sooner reached, as for example, $\text{Ag}(\text{CN})_3\text{K}$, $\text{Cu}(\text{CN})_3\text{K}$.

It is according to the same idea that the complex acids of molybdenum, tungsten, etc., are to be explained, where a large number of the oxide groups are polymerized together in stable form. Just what may be the structure of such highly polymerized groups it is now not possible to say, beyond that in all probability it is spacial.

We have thus sketched the features of Werner's theory, which is necessarily incomplete. It has required more than half a century to bring the valence theory to its present form, and yet, when it reaches the structure of molecular compounds, in by far the greater number of such compounds, it utterly breaks down.

It remains to point out some of the weaknesses of the application of the valence theory to some of these molecular compounds. In its application to the metal-ammonia salts the theory in the hands of Jörgensen, who in this field is master, has two weak points. First, while it applies well to the more stable of these bases, as those of cobalt, chromium, platinum, etc., the same principles are not applicable to the less stable of these ammonia compounds as those of copper, zinc, nickel, etc., yet the chemical difference between these compounds is not one of kind but of degree. Nor does it

take any possible cognizance of the fact that in many of these less stable ammonia compounds, the ammonia can be replaced in part or in whole by water. It is a theory which applies to only one particular class of ammonia compounds. Second, it

assumes the existence of the group $\begin{array}{c} \text{H, H, H, H,} \\ \text{—N—N—N—N—} \end{array}$ and even the group $\begin{array}{c} \text{H, H, H, H,} \\ \text{—N—N—N—N—} \end{array}$ in stable compounds.

Now from what we know of the nitrogen atom, such a group would necessarily be exceedingly unstable. Even compounds of two nitrogen atoms united N—N are far from stable, and it is hardly conceivable that the N₄ group should be of such remarkable stability. Since, however, there is no limit to the substitution of ammonia groups by water we are

led to a formula of $\begin{array}{c} \text{H}_2\text{O—Cl} \\ \text{Cr—H}_2\text{O—Cl} \\ \text{H}_2\text{O—H}_2\text{O—H}_2\text{O—H}_2\text{O—Cl} \end{array}$ for the hydrated aluminum chloride, which would hardly be agreed to by the most pronounced adherent of the valence theory.

To explain the double chlorides according to the valence theory Remsen has used a development of the Blomstrand theory, assuming the bivalent groups Cl₂, F₂, thus:

$\begin{array}{c} \text{Cl=Cl—K} \\ \text{Fe—Cl=Cl—K} \end{array}$, etc. So long as the number of the alkaline salt molecules is no greater than that of the halogen atoms in the halide, this explanation might serve, but when this number becomes greater, as is sometimes the case, it becomes

necessary to assume the trivalent Cl₃ group, as $\begin{array}{c} \text{Cl—K} \\ \text{Cu—Cl—Cl—K} \end{array}$

for $\text{CuCl}_2.2\text{KCl}$ and $\begin{array}{c} \text{Cl—K} \\ \text{Cd—Cl—Cl—K} \\ \text{Cl—K} \end{array}$ for $\text{CdCl}_2.4\text{KCl}$. But this

explanation covers only the double halides. The double cyanides and double nitrites which it is reasonable to consider are analogous, must be otherwise accounted for.

The efforts to elucidate the structure of the double cyanides have been many but unsatisfactory. Graham assumed in the double iron cyanides the special trivalent group (CN)₃; Blomstrand used his chain formulæ; Erlenmeyer using Gra-

ham's $(\text{CN})_6$, gives it the structure

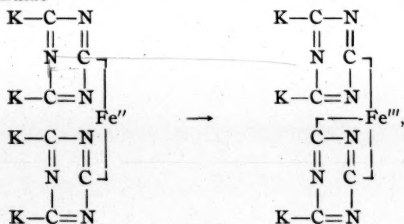
$$\begin{array}{c} \leftarrow \text{C}-\text{N} \\ || \quad || \\ \text{N} \quad \text{C} \rightarrow \\ | \quad | \\ \leftarrow \text{C}=\text{N} \end{array}, \text{ while others}$$

have suggested

$$\begin{array}{c} \leftarrow \text{C}=\text{N} \\ | \quad | \\ \text{N}-\text{C} \rightarrow \\ | \quad | \\ \leftarrow \text{C}=\text{N} \end{array}.$$

Aside from the improbability

of representing the change of $\text{K}_4\text{Fe}(\text{CN})_6$ into $\text{K}_3\text{Fe}(\text{CN})_6$ by the formulae



thus writing the two $(\text{CN})_6$ groups differently with the iron and potassium, there stand, first, Freund's conversion of hy-

drogen ferrocyanide into the imido ether, $\text{H}_4\text{FeC}_2 \begin{array}{l} (\text{NH})_2 \\ (\text{OC}_2\text{H}_5)_2 \end{array}$,

where each cyanogen group has acted independently, and, second, the existence of the nitroprussides so-called, where one of the six cyanogens is replaced by the nitroso group.

Even if these explanations were all satisfactory in themselves, there would still be the objection that many obviously related and often closely related compounds are explained on various different principles.

I have not attempted to touch on the development of Werner's theory in its interesting application of stereoisomerism to inorganic compounds save in a single instance, from the fact that there is still too much doubt about those cases which are possibly to be included in this field. Nor have I touched upon the objections to the theory especially as urged by Jørgensen. These objections seem to me to attack its application to special compounds, and especially to those compounds whose doubtful isomerism, as well as constitution, are not essential to the theory. I do not think that valid objections to the theory in its larger lines have yet been brought forward.

It is true that the conception of the coordinated group is one new and strange to our present chemical ideas, but the same was true of the electrolytic dissociation of salts in solution, and the idea of a free ion is still difficult for some of us to grasp. Of the nature of valence itself we know little or nothing, and it is by no means impossible that, if the nature of valence were known to us, the nature of coordination would also become clear.

Werner's theory is doubtless not the whole truth, but it seems to me that there is truth in it and that it is a distinct step, and the first that has been taken to bring the vast number of inorganic compounds (and perhaps organic as well) in one category, to unify our science. It is in its present form crude, as with most new theories; much remains to be done. The multifarious classes of complex compounds must be studied in their relation to the theory and relegated to their proper type, and these types must be studied in their relation to the periodic system. I cannot better close this imperfect review than by quoting from Werner: "The modern doctrine of the constitution of chemical compounds, worked out in such a wonderful way, the doctrine of the inner structure of the molecule, is based upon a knowledge of the valence of the elements, and hence has taken a characteristic trend. It is the doctrine of the constitution of valence compounds. In unfortunate contrast to the thorough development of this, stands the development of the doctrine of the constitution of molecular compounds; and this is the case chiefly because the idea of valence fails when applied to these compounds. Practically, the only molecular compounds of which the modern doctrine of chemical constitution takes cognizance, are those for which, by the help of lines and 'bonds,' a meager and questionable valence formula can be pictured." Let us hope that the near future will give us a broader view.

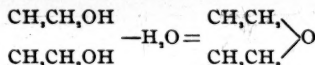
JAS. LEWIS HOWE.

References to Werner's Theory of the Constitution of Inorganic Compounds.

Ztschr. anorg. Chem., **3**, 267; **5**, 147; **7**, 108, 289; **8**, 153, 189; **9**, 382; **10**, 320; **11**, 254, 416; **13**, 172, 211; **14**, 21, 263, 367, 404; **15**, 1, 123, 143, 243; **16**, 109, 244, 377, 398; **17**, 35, 82, 480; **18**, 152, 253; **19**, 106, 109, 158; **21**, 96, 145. Ber. d. chem. Ges., **28**, 1489, 1493.

SCHOOL CHEMISTRY. BY CHARLES BASKERVILLE, PH.D., The University of North Carolina. Richmond, Virginia: B. F. Johnson Publishing Co. 1899. 159 pages.

In the preface the author says "The material * * * has been adapted to the needs of the schools in the Southern States." "A large part of the ninety per cent of high school graduates, who do not secure a college or university training, never learn a chemical principle or fact except by accident. The course presented is not intended to replace college work, but seeks that class of people mentioned." The author has fallen into the error, which is so common in books of this kind, of trying to cover the whole field in a few lessons. Would it not be far better to study a few typical substances thoroughly, rather than to have one thing after another mentioned in a brief unsatisfactory way. The theoretical part, as it must necessarily be in such a work, is a mere statement of facts which cannot make the desired impression without a clear presentation of the reasons upon which the deductions are based. The atomic theory is explained (?) in about a dozen lines in the early part of the book, while the laws of definite and multiple proportions are not mentioned until much later. What impression does it make on one who has only had twenty lessons when he is told that if "we subtract a molecule of water from two molecules of alcohol, we have



a body called an ether." "Sulphuric acid has the power of tearing water away from certain substances, hence we may use that reagent for removing water from alcohol to produce ether."

The author says that this book is the outcome of five years' experience as a teacher in a summer school for teachers. It is an unfortunate system which necessitates such books as compendiums and condensed works for those who imagine they can successfully complete a year's work in a few weeks.

J. E. G.

DIE LEHRE VON DER ELEKTRIZITÄT. BY GUSTAV WIEDEMANN. Second, revised and enlarged, edition. Vol. IV. Large 8vo. xiii + 1237 pp. Braunschweig: F. Vieweg & Sohn, 1898. Price, 32 marks.

It is very fortunate that the fourth and concluding volume of Wiedemann's great handbook of electricity was completed before the author's recent death. The volume treats induction, the absolute measure of electrical quantities, and the hypothetical views that have been held regarding electricity and

its mode of action. But little of this has a direct bearing upon chemistry. The chief items of interest are, probably, the reports upon the resistance offered by electrolytes to currents induced by electric waves; and upon the relation between chemical composition and dielectric constant, as studied by Thwing, Landolt and John, Nernst, Drude, and others. The concluding chapter has, of course, an interest for the general reader. It is announced that a subsidiary volume, by Eilhard Wiedemann, will be devoted to the conduction of electricity by gases.

J. E. T.

THE ELEMENTS OF BLOWPIPE ANALYSIS. BY F. H. GETMAN, F. C. S., Instructor in Chemistry in the Stamford High School. New York: The Macmillan Co. 1899. 77 pages. 60 cents.

This book is intended for use in high schools and colleges and is designed to give the student a general outline of blowpipe analysis, and to introduce him to the methods of determinative mineralogy. The material has been simplified as much as possible and tables for 'systematic' examination have been omitted. After describing the methods of work, the author takes up each element in turn and gives its behavior, or leaves it blank to be filled out by the student, when heated alone on platinum wire or with various reagents. The reactions of some of the principal ores are also given.

J. E. G.

LABORATORY MANUAL. Experiments to Illustrate the Elementary Principles of Chemistry. BY H. W. HILLYER, PH.D., Assistant Professor of Organic Chemistry in the University of Wisconsin. New York. The Macmillan Co. 1899. 200 pages. 90 cents.

This book can be highly recommended as a laboratory guide for those beginning the study of chemistry. The experiments are arranged in a logical order and are very clearly presented. The student is not, as is so often the case, compelled to go far beyond his depth at the first step, but he feels his way slowly and carefully, getting a firm foundation from a thorough study of a few of the simpler elements before taking up more difficult problems. For those students who, from a course in some preparatory school, are in a position where it would be unprofitable to follow the exact course designed for beginners, and who, on the other hand, are not fitted to pursue a more advanced course, the author has introduced some supplementary experiments throughout the book and also some simple quantitative experiments. The experiments are printed on only one side of the page, the other being blank for the results of the experiments.

J. E. G.

THE NEWER REMEDIES. BY VIRGIL COBLENTZ, A.M., Phar.M., Ph.D., F.C.S., Etc., Professor of Chemistry and Physics in the New York College of Pharmacy. Third Edition. Philadelphia: P. Blakiston's Son & Co. 1899. Price, \$1.00.

Questions concerning the composition and properties of the new remedies, which are almost daily introduced, are constantly being put to the chemist and the pharmacist, and frequently they cannot answer them, as it is impossible to keep thoroughly informed on the subject. In most cases no idea of the composition can be obtained from the name, and when we consider that about 1200 of these remedies have been introduced in the last three years, the hopelessness of the problem is better realized. The author has come to our aid with this book, in which he has collected several thousand of the new remedies arranged in alphabetical order with the methods of preparation, tests, solubilities, doses, and other properties which may be of interest. It is a valuable reference book on this subject, and is published in a handy and neat form.

J. E. G.